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NUTRIENT REMOVAL AND ADVANCED WASTE TREATMENT. ADVANCED WASTE TREATMENT SEMINAR HELD AT PORTLAND, OREGON ON FEBRUARY 5 AND 6, 1969

E. F. Barth

Federal Water Pollution Control Administration
Portland, Oregon

1969

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A TECHNICAL SEMINAR

CLEAN WATER

NUTRIENT REMOVAL
and
ADVANCED WASTE
TREATMENT

Lloyd Center Auditorium
Portland, Oregon

February 5-6, 1969

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FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
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FORMS AND MEASUREMENT
OF
NITROGEN AND PHOSPHORUS

E. F. Barth

ADVANCED WASTE TREATMENT SEMINAR
Portland, Oregon
February 5 and 6, 1969

3-1-

This topic will consider the general chemistry of nitrogen and phosphorus from a treatment and control standpoint.

Nitrogen and phosphorus form many similar type compounds, but there are important differences.

Because of the reagents and procedural operations involved in the determination of phosphorus careful analytical control is necessary.

The reagents and test condition for various nitrogen forms are usually very specific. However, because of the complex biological transformations of nitrogen, all forms must be measured.

The most comprehensive review of phosphorus determinations in water is:

Sigurd Olsen, "Determination of Orthophosphate in Water."

Proceeding of I.B.P. Symposium Chemical Environment In The Aquatic Habitat. Published by N.V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, 1967.

The following is a list of slides that will be used to present the topic.

1. Periodic Table
2. Phosphorus and Biological Treatment
3. Determination of Various Phosphorus Forms
4. Fractions of Various Phosphorus Forms
5. Compounds of Phosphorus
6. Solubilities of Phosphorus Compounds
7. Effect of Acid Concentration on Molybdate Color
8. Biological Transformations of Nitrogen
9. Nitrogen Removal Efficiency
10. Van Slyke Reaction

PERIODIC TABLE OF THE ELEMENTS
FIGURE 1

SUBSHELLS BEING COMPLETED

s d s p

LIGHT METALS

TRANSITION HEAVY METALS

NON METALS

INEPT GASES

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	INEPT GASES
1 1 H 1.0080	2 2 He 4.003																2 2 He 4.003
2 1 3 Li 6.940	2 2 4 Be 9.013											2 3 5 B 10.82	2 4 6 C 12.011	2 5 7 N 14.008	2 6 8 O 16.000	2 7 9 F 19.00	2 8 10 Ne 20.183
2 8 1 11 Na 22.991	2 8 2 12 Mg 24.32											2 8 3 13 Al 26.98	2 8 4 14 Si 28.09	2 8 5 15 P 30.975	2 8 6 16 S 32.066	2 8 7 17 Cl 35.457	2 8 8 18 Ar 39.944
2 8 8 1 19 K 39.100	2 8 8 2 20 Ca 40.08	2 8 9 2 21 Sc 44.96	2 8 10 2 22 Ti 47.90	2 8 11 2 23 V 50.95	2 8 13 1 24 Cr 52.01	2 8 13 2 25 Mn 54.94	2 8 14 2 26 Fe 55.85	2 8 15 2 27 Co 58.94	2 8 16 2 28 Ni 58.71	2 8 18 1 29 Cu 63.54	2 8 18 2 30 Zn 65.38	2 8 18 3 31 Ga 69.72	2 8 18 4 32 Ge 72.60	2 8 18 5 33 As 74.91	2 8 18 6 34 Se 78.96	2 8 18 7 35 Br 79.916	2 8 18 8 36 Kr 83.80
2 8 18 8 1 37 Rb 85.48	2 8 18 8 2 38 Sr 87.63	2 8 18 9 2 39 Y 88.92	2 8 18 10 2 40 Zr 91.22	2 8 18 12 1 41 Nb 92.91	2 8 18 13 1 42 Mo 95.95	2 8 18 13 2 43 Tc (99)	2 8 18 15 1 44 Ru 101.1	2 8 18 15 1 45 Rh 102.91	2 8 18 18 46 Pd 106.4	2 8 18 18 1 47 Ag 107.880	2 8 18 18 2 48 Cd 112.41	2 8 18 18 3 49 In 114.82	2 8 18 18 4 50 Sn 118.70	2 8 18 18 5 51 Sb 121.76	2 8 18 18 6 52 Te 127.61	2 8 18 18 7 53 I 126.91	2 8 18 18 8 54 Xe 131.30
2 8 18 18 8 1 55 Cs 132.91	2 8 18 18 8 2 56 Ba 137.36	57-71 See Lanthanide Series	2 8 18 32 10 2 72 Hf 178.50	2 8 18 32 11 2 73 Ta 180.95	2 8 18 32 12 2 74 W 183.86	2 8 18 32 13 2 75 Re 186.22	2 8 18 32 14 2 76 Os 190.2	2 8 18 32 15 2 77 Ir 192.2	2 8 18 32 17 1 78 Pt 195.09	2 8 18 32 18 1 79 Au 197.0	2 8 18 32 18 2 80 Hg 200.61	2 8 18 32 18 3 81 Tl 204.39	2 8 18 32 18 4 82 Pb 207.21	2 8 18 32 18 5 83 Bi 209	2 8 18 32 18 6 84 Po 210	2 8 18 32 18 7 85 At (210)	2 8 18 32 18 8 86 Rn 222
2 8 18 32 18 8 1 87 Fr (223)	2 8 18 32 18 8 2 88 Ra 226.05	89-100 See Actinide Series															

d f

6 P	LANTHANIDE SERIES (Rare Earth Elements)	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm (147)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
7 Q	ACTINIDE SERIES	89 Ac (227)	90 Th 232.05	91 Pa (231)	92 U 238.07	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk 249	98 Cf (251)	99 Es 254	100 Fm (253)	101 Md 256	102 No (254)	

PHOSPHORUS IS DIFFERENT

ELEMENT	BIOLOGICAL REACTION	RESULT OF TREATMENT NET LOSS
OXYGEN	OXIDATION AND/OR REDUCTION	CO_2 CH_4
CARBON		
HYDROGEN		H_2 H_2O
NITROGEN		N_2
SULFUR		H_2S
		NO LOSS
PHOSPHORUS	NO OXIDATION NO REDUCTION	ORGANIC PHOSPHORUS ⇅ INORGANIC PHOSPHORUS

TABLE I

Determination of Various Phosphorus Forms

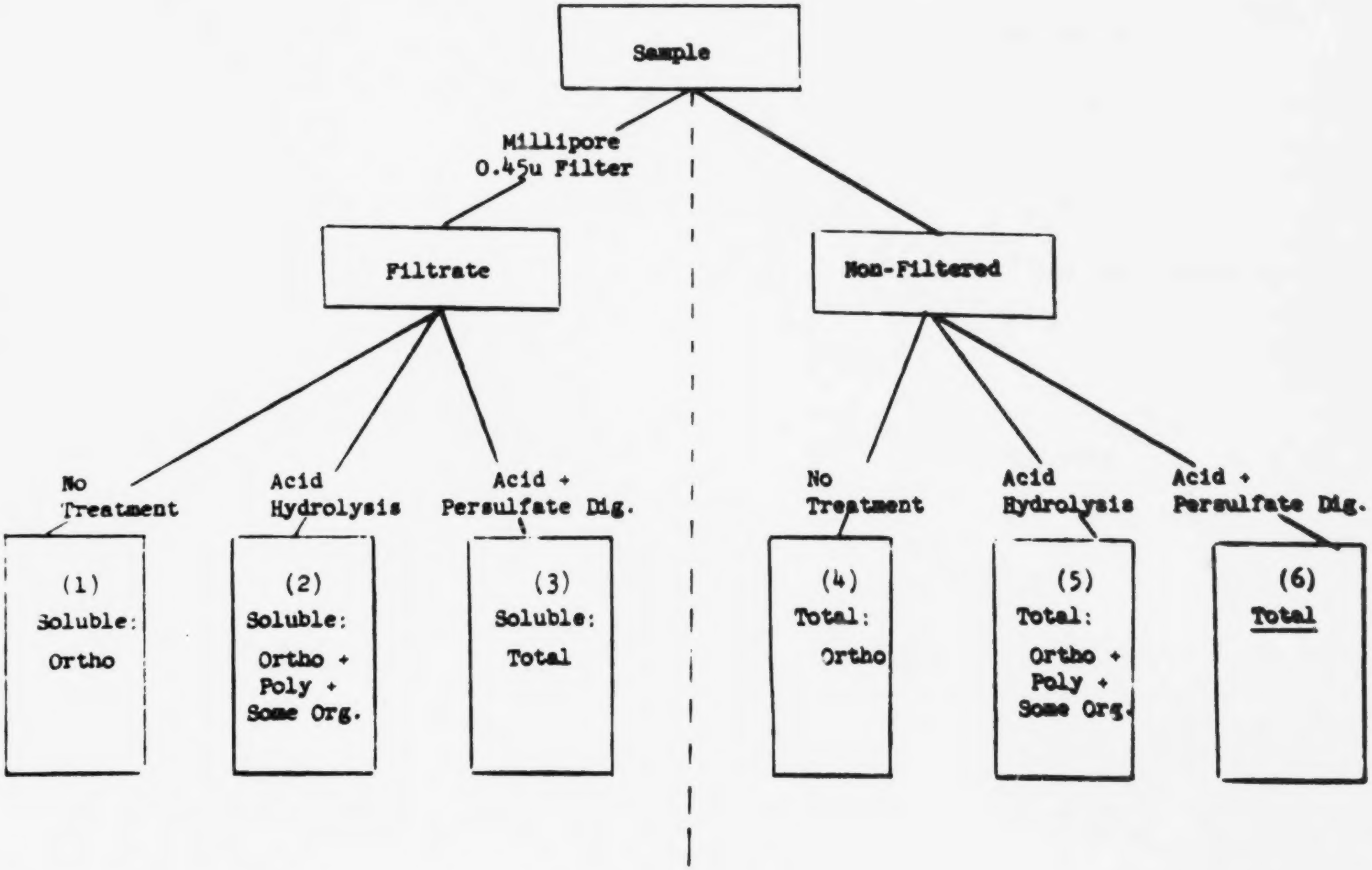
Sample
Millipore 0.45u Filter
Filtrate
Non-Filtered
No Treatment
Acid Hydrolysis
Acid + Persulfate Dig.
No Treatment
Acid Hydrolysis
Acid + Persulfate Dig.
(1) Soluble: Ortho
(2) Soluble: Ortho + Poly + Some Org.
(3) Soluble: Total
(4) Total: Ortho
(5) Total: Ortho + Poly + Some Org.
(6) Total

TABLE II

Data Treatment	Phosphorus Components Determined
	A. Soluble Forms
1	1) ortho
2	2) ortho + poly + some org's.
3	3) total
2 - 1	4) poly + some org's.
3 - 2	5) most org's.
	B. Total Forms
4	6) ortho
5	7) ortho + poly + some org's.
6	8) total
5 - 4	9) poly + some org's.
6 - 5	10) most org's.
	C. Particulate Forms
4 - 1	11) ortho
(5-4) - (2-1)	12) poly + some org's.
(6-5) - (3-2)	13) most org's.
6 - 3	14) total

TABLE III

Forms and Measurements of Phosphorus

Phosphoric Anhydride	P_4O_{10} (usually calculated as P_2O_5)

Orthophosphates Found in Water

Phosphoric acid	H_3PO_4 below pH 2.2
Dihydrogen phosphate ion (monovalent)	$H_2PO_4^-$ from pH 2.2 to 7.2
Monohydrogen phosphate ion (divalent)	$HPO_4^{=}$ from pH 7.2 to 12.4
Phosphate ion (trivalent)	$PO_4^{\equiv}$ above pH 12.4
Dicalcium phosphate	$CaHPO_4$ from pH 6 to 8

(Tricalcium phosphate, $Ca_3(PO_4)_2$, does not form in water)

Hydroxyapatite	$Ca_5OH(PO_4)_3$ above pH 7-8
Fluorapatite	$Ca_5F(PO_4)_3$ above pH 7

Aluminum hydroxide adsorbs $HPO_4^{=}$ from pH 5 to 10

Aluminate ion $Al(OH)_4^-$ forms above pH 10

Ferric hydroxide adsorbs $HPO_4^{=}$ above pH 4

Magnesium hydroxide flocculates colloidal phosphates above pH 10-11

Polyphosphates

All polyphosphates hydrolyze slowly to orthophosphates

Sodium Trimetaphosphate	$Na_3(PO_3)_3$ -- a ring compound
Sodium Polymetaphosphate	$(NaPO_3)_n$ -- a long chain

(there is no justification for the name "hexametaphosphate")

Sodium Pyrophosphate	$Na_4P_2O_7$
Sodium Tri Polyphosphate	$Na_5P_3O_{10}$

Organic Phosphates

Esters and anhydrides	$ROPO_3^{=}$, $ROPO_3PO_3^{=}$
Phosphagens	$RNPO_3^{=}$

Reference

(1) Van Wazer, J. R. Phosphorus and Its Compounds. Interscience 1958.

TABLE IV

PHOSPHORUS COMPOUNDS CLASSIFIED BY CHEMICAL AND SOLUBILITY RELATIONS(1)

Form	Water Soluble(2)	Insoluble(2)
1. Ortho phosphates $(PO_4)^{-3}$	Combined with monovalent cations such as H, Na, K, NH_4	Combined with multi valent cations such as $CA^{+2}Al^{+3}Fe^{+3}$
2. Poly phosphates $(P_2O_7),^{-4}(P_3O_{10})^{-5}(P_3O_9)^{-3}$ and others depending upon the degree of dehydration.	(a) as in 1 (above), but solubility decreases as molecular weight increases	(a) as in 1 (above) (b) multi P polyphosphates (high mol. wt.) including the "glassy" phosphates
3. Organic phosphorus R-P, R-P-R (3) (unusually varied nature)	(a) certain chemicals (b) degradation products (c) enzyme P (d) phosphorylated nutrients	(a) certain chemicals (b) cell mass, may be colloidal or agglomerated (c) soluble P sorbed by insoluble residues
4. Mineral phosphorus	(a) as in 1 (above), but solubility decreases for complex forms	(a) as in 1 (above) (b) geological P such as phosphosilicates (c) certain mineral complexes

(1) Table drawn from a lecture, "Determination of Phosphorus in the Aqueous Environment," by F. Ludzack, FWPCA Training Activities, Ohio Basin Region.

(2) Used to indicate usual state under common conditions.

(3) R represents an organic radical, P represents P, PO_4, or its derivatives.

TABLE V

Effect of Varing Sulfuric Acid - Ammonium Molybdate Ratio on Heteropoly Blue Color Development
(Stannous chloride in glycerine reductant)

Acid Molybdate Reagent Composition		Normality* of acid in final 100 ml assay volume	Absorbancy (O.D.)	
Ammonium Molybdate gm/100 ml	Concentrated Sulfuric Acid ml/100 ml		Distilled Water	0.05 mg P Standard
2.0	5	0.072	> 2.0	> 2.0
2.0	10	0.144	0.805	1.00
2.0	15	0.216	0.260	0.580
2.0	20	0.288	0.036	0.475
2.0	25	0.360	0.004	0.415
2.0	30	0.432	0.000	0.365
2.0	35	0.504	0.000	0.345
2.0	40	0.576	0.000	0.252
2.0	50	0.720	0.000	0.060
2.0	60	0.864	0.000	0.012

*Calculated normality of H_2SO_4 in the 100 ml final volume produced by using 4.0 ml of the particular acid molybdate solution.

Figure 8
Nitrogen Transformations

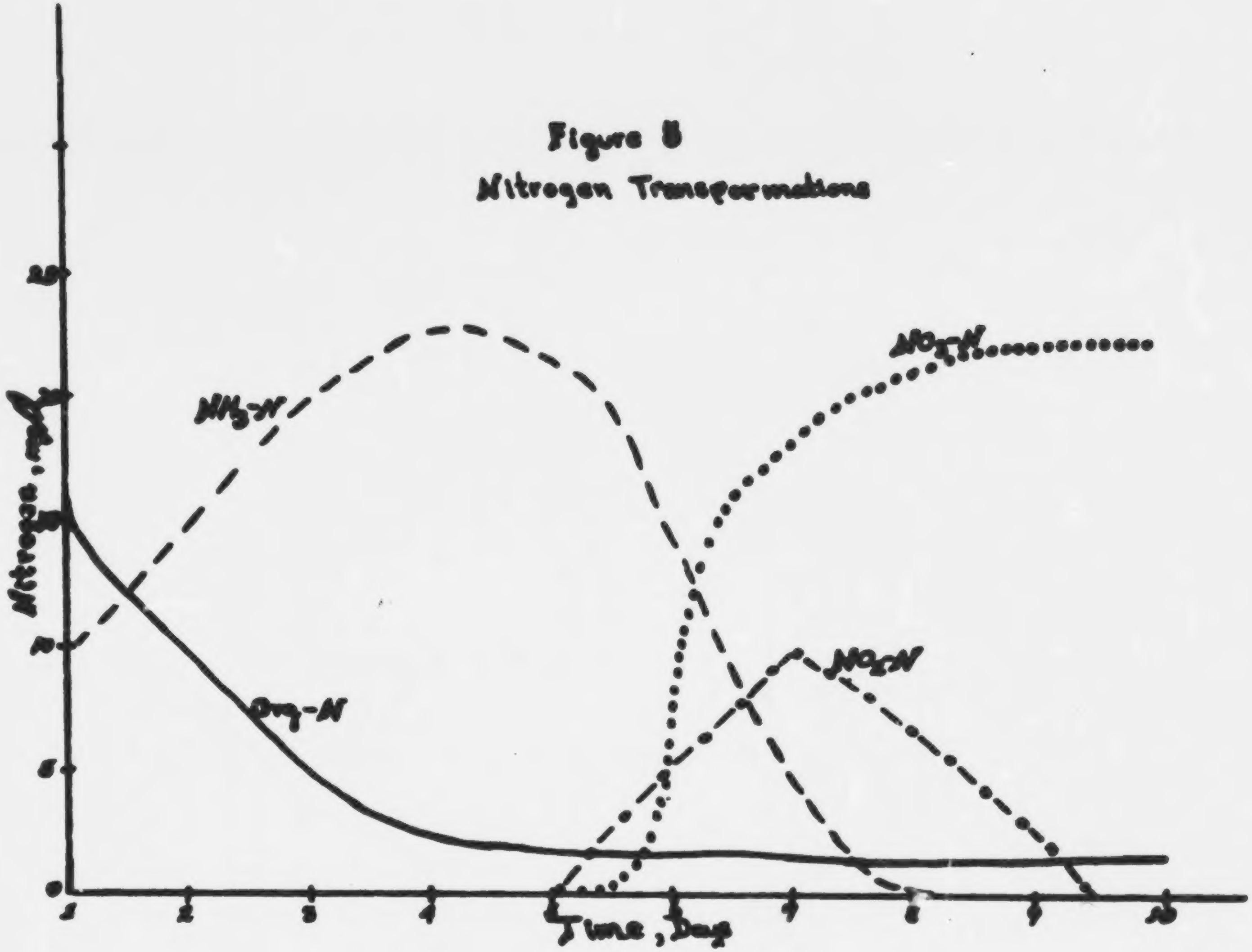

TABLE VI

Nitrogen Forms in 1:1 Mixture of High-Rate and Nitrified Effluents

Nitrogen Form	High-Rate Effluent	Nitrified Effluent		Denitrified Effluent		Oxidized Nitrogen Removal	Over-All Removal
Organic-N	5	2		3			
Ammonia-N	10	0		5			
NO_2-N	-	1	13	0.5	1.0		
NO_3-N	-	12		0.5		92%	
Sum	15	15		9			40%

FIGURE 4

VAN SLYKE REACTION

$$RNH_2 + NO_2^- \xrightarrow{acid} ROH + N_2\uparrow + H_2O$$

PRESENT AND PROJECTED PHOSPHORUS REMOVAL
IN CONVENTIONAL TREATMENT

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PRESENT AND PROJECTED PHOSPHORUS REMOVAL
IN CONVENTIONAL TREATMENT

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February 5 and 6, 1969

This discussion will indicate the magnitude of the phosphorus problem, some of the shortcomings of our treatment and collection systems, and the biological cycle of phosphorus in nature.

Many investigators have considered various means of controlling phosphorus; these will be discussed and the three approaches currently in practice will be briefly described.

The parameters thought necessary for biological removal of phosphorus will be presented, and the flow sheet for a treatment plant specifically designed for biological uptake will be shown.

Substantial improvement in conventional treatment could be obtained by breaking the cycle [illegible] digester supernatant. Progress along this line will be presented.

The following slides will be used, and where available, a reproduction of the slide is attached:

Slide No.	Title
1	Population with Waste Treatment Systems 1962
2	Treatment Classification by Population 1962

3 Treatment Classification by Facilities 1962

4 Phosphorus Removal by Conventional Treatment Systems

5 Estimate of Total Amount of Phosphorus Discharged to Water System

6 Cycle of Phosphorus in Nature

7 Various Approaches to Phosphorus Control

8 Three Main Approaches

9 Flow Diagram of Approaches

10 Parameters Deemed Necessary for Biological Removal of Phosphorus

11 Design of a Phosphorus Removal Biological Treatment Plant

12 Characteristics of Digester Supernatant

13 Digester Supernatant Process

POPULATION WITH WASTE SYSTEMS FOR YEAR 1962

186×10^6	Total population
118×10^6	Total sewered (63%)
104×10^6	Receive treatment
	83% of sewered
	56% of total

TREATMENT CLASSIFICATION BY POPULATION FOR YEAR 1962

Population	Type of treatment	% of treated	% of of total
38×10^6	Primary-intermediate	37	20
33×10^6	Activated sludge	32	18
23×10^6	Trickling filter	22	12
10×10^6	Other	9	6

TREATMENT CLASSIFICATION BY FACILITIES FOR YEAR 1962

Number	Type	% of total
11,655	Total	100
2,277	Raw discharge	19.5
9,378	Treated discharge	80.5
2,794	Primary-intermediate	24.0
6,584	Secondary	56.5
800	Activated sludge (12% of secondary)	7.0
3,506	Trickling filters (53% of secondary)	30.0
1,348	Stabilization ponds (20% of secondary)	12.0

PHOSPHATE REMOVAL BY WASTEWATER TREATMENT PLANTS

Type	% removal
Primary sedimentation	5-15
Extended aeration (sludge wasting)	8-15
Trickling filter	20-30
Activated sludge	30-50

Figure II

ESTIMATE OF TOTAL AMOUNT OF PHOSPHORUS DISCHARGED TO WATER SYSTEM

Per capita contribution of phosphorus is 4 pounds per person per year

Population x per capita x efficiency	Pounds discharged
Not served by any treatment $70 \times 10^6 \times 4 \times 0.00$	280×10^6
Served by primary treatment only $40 \times 10^6 \times 4 \times 0.10$	154×10^6
Served by trickling filter or extended aeration $30 \times 10^6 \times 4 \times 0.25$	90×10^6
Served by activated sludge $40 \times 10^6 \times 4 \times 0.40$	96×10^6
Total pounds of phosphorus discharged to water system per year	610×10^6

BALANCE BETWEEN HETEROTROPHIC AND AUTOTROPHIC GROWTH (Stumm & Tenney, 1963)

Treatment Plant

Wastewater contains organic and inorganic C-H-O-N-P. By heterotrophic activity this is converted to CO_2, H_2O, NO_3, PO_4. A large portion of oxygen demand is satisfied by conversion to CO_2, but N and P are solubilized and enter receiving stream.

Receiving Stream

$$1\ PO_4 + \text{light energy} \xrightarrow[\text{Autotrophic activity}]{CO_2,\ N} 154\ O_2 + C_{106}H_{180}O_{45}N_{16}P_1$$

The Cycle

$1\ \#\ \text{Phosphorus} \rightleftharpoons 75\ \#\ \text{of algae} \rightleftharpoons 160\ \#\ O_2$

A steady state exists in the overall environment of the earth. There is always excess O_2 in the atmosphere.

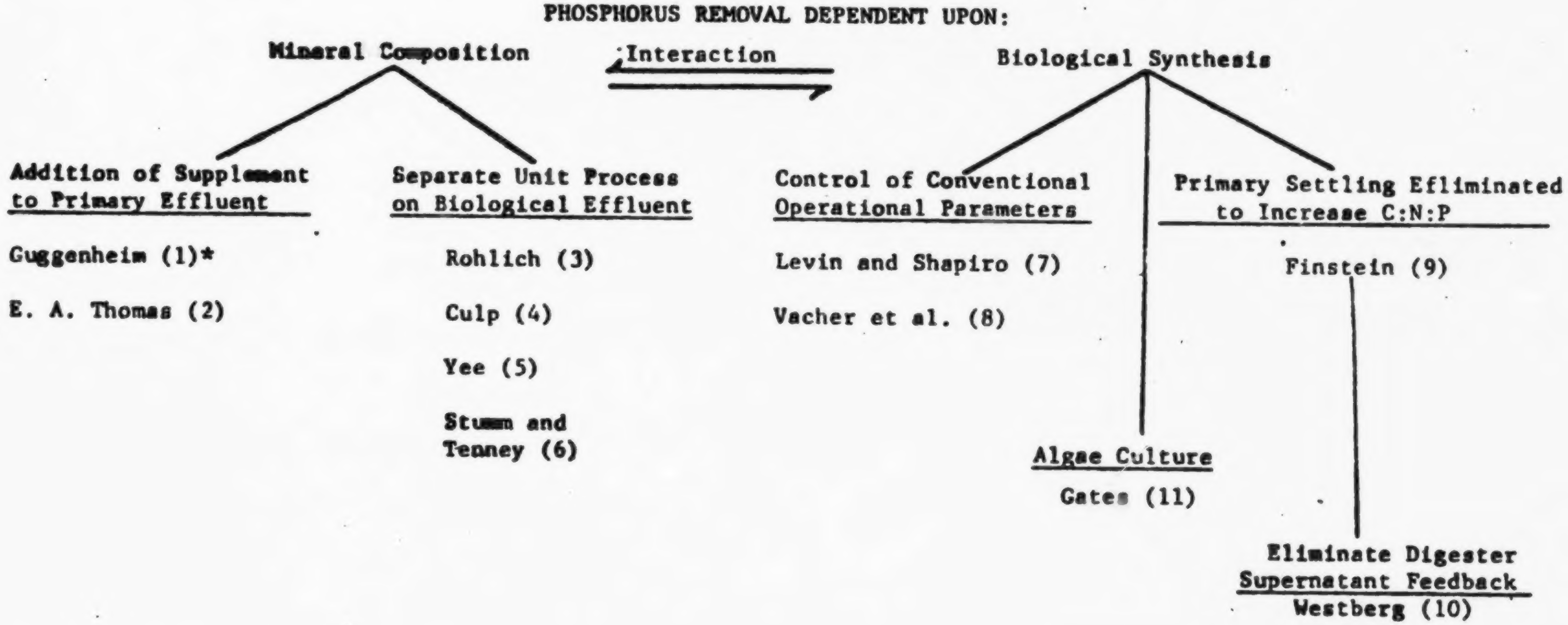
In localized environments pollution results from an imbalance.

Excess heterotrophic activity = DO depletion caused by excess organic matter.

Excess autotrophic activity = large algal mass produced caused by excess inorganic matter.

FIGURE I

Phosphorus Removal by Wastewater
Treatment (Excluding Lagoons and Percolation)


PHOSPHORUS REMOVAL DEPENDENT UPON:
Mineral Composition
Interaction
Biological Synthesis
Addition of Supplement to Primary Effluent
Guggenheim (1)*
E. A. Thomas (2)
Separate Unit Process on Biological Effluent
Rohlich (3)
Culp (4)
Yee (5)
Stumm and Tenney (6)
Control of Conventional Operational Parameters
Levin and Shapiro (7)
Vacher et al. (8)
Algae Culture
Gates (11)
Primary Settling Efliminated to Increase C:N:P
Finstein (9)
Eliminate Digester Supernatant Feedback
Westberg (10)

*( ) indicates literature reference.

TABLE III. APPROACHES TO PHOSPHORUS REMOVAL

CONTROL OF BIOLOGICAL UPTAKE

CHEMICAL TREATMENT OF BIOLOGICAL EFFLUENT OR PROCESS STREAM TO FORM SLIGHTLY SOLUBLE PHOSPHORUS COMPOUNDS

COMBINATION OF THESE TWO ABOVE APPROACHES

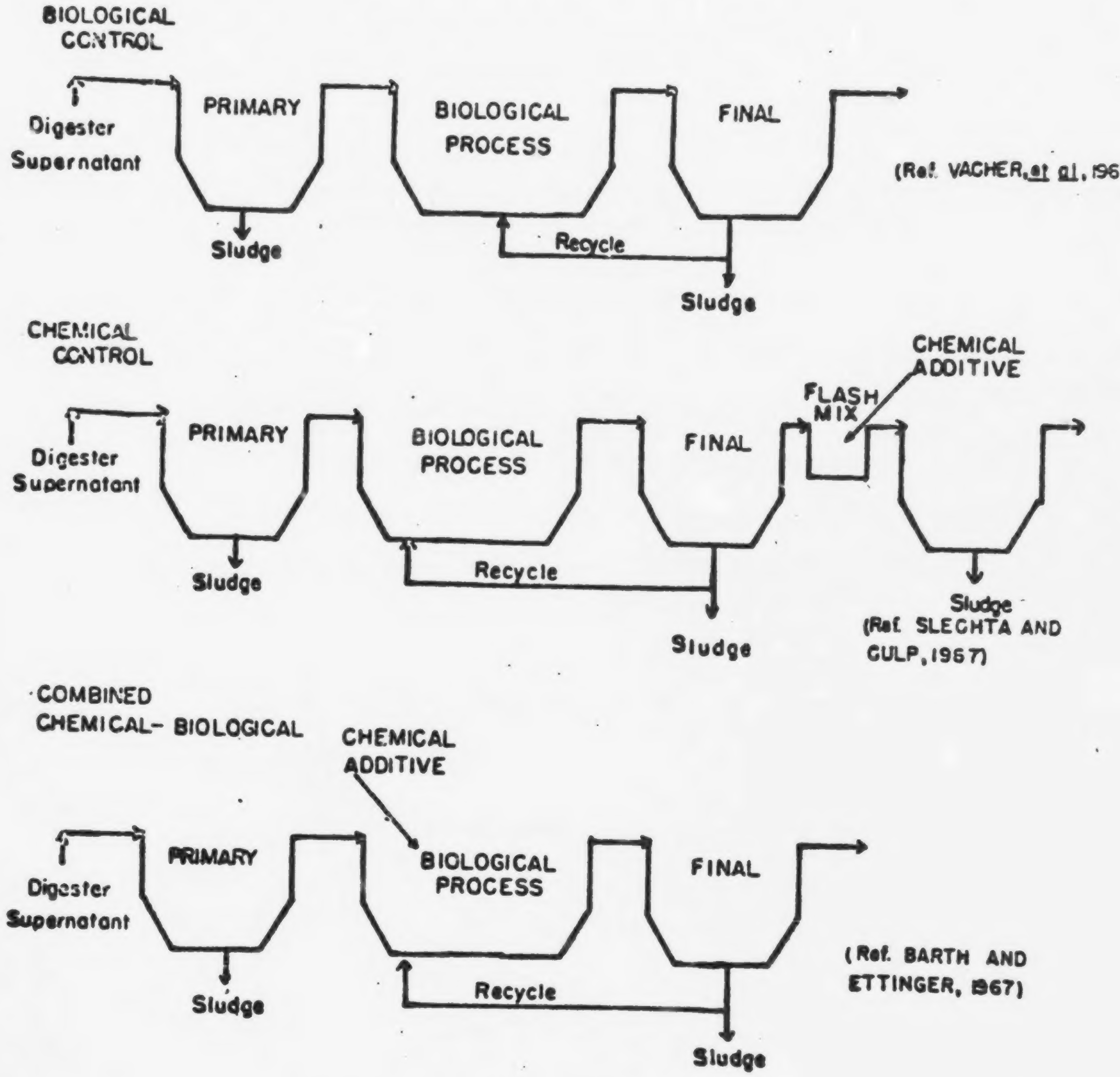

BIOLOGICAL CONTROL
Digester Supernatant
PRIMARY
BIOLOGICAL PROCESS
FINAL
Sludge
Recycle
Sludge
(Ref. VACHER, et al, 1967)
CHEMICAL CONTROL
Digester Supernatant
PRIMARY
BIOLOGICAL PROCESS
FINAL
FLASH MIX
CHEMICAL ADDITIVE
Sludge
Recycle
Sludge
Sludge
(Ref. SLECHTA AND CULP, 1967)
COMBINED CHEMICAL- BIOLOGICAL
CHEMICAL ADDITIVE
Digester Supernatant
PRIMARY
BIOLOGICAL PROCESS
FINAL
Sludge
Recycle
Sludge
(Ref. BARTH AND ETTINGER, 1967)

FIGURE I. PHOSPHORUS CONTROL BASIC SYSTEMS

PARAMETERS DEEMED NECESSARY FOR EFFICIENT BIOLOGICAL REMOVAL OF PHOSPHORUS

1. Eliminate Digester Supernatant Recycle
2. Aeration Time and Rate of Air Supply
3. Concentration of Mixed Liquor Suspended Solids
4. Concentration of Dissolved Oxygen in Aerator
5. Period of Sludge Retention in Secondary Clarifier
6. Additional Benefit Possible by Stripping of Phosphorus from Return Sludge
    a) Anaerobic Stripping
    b) Acid Stripping

Greater Manassas Sanitary District
1 m.g.d.

NO PRIMARY SEDIMENTATION
TREATED DIGESTER SUPERNATANT

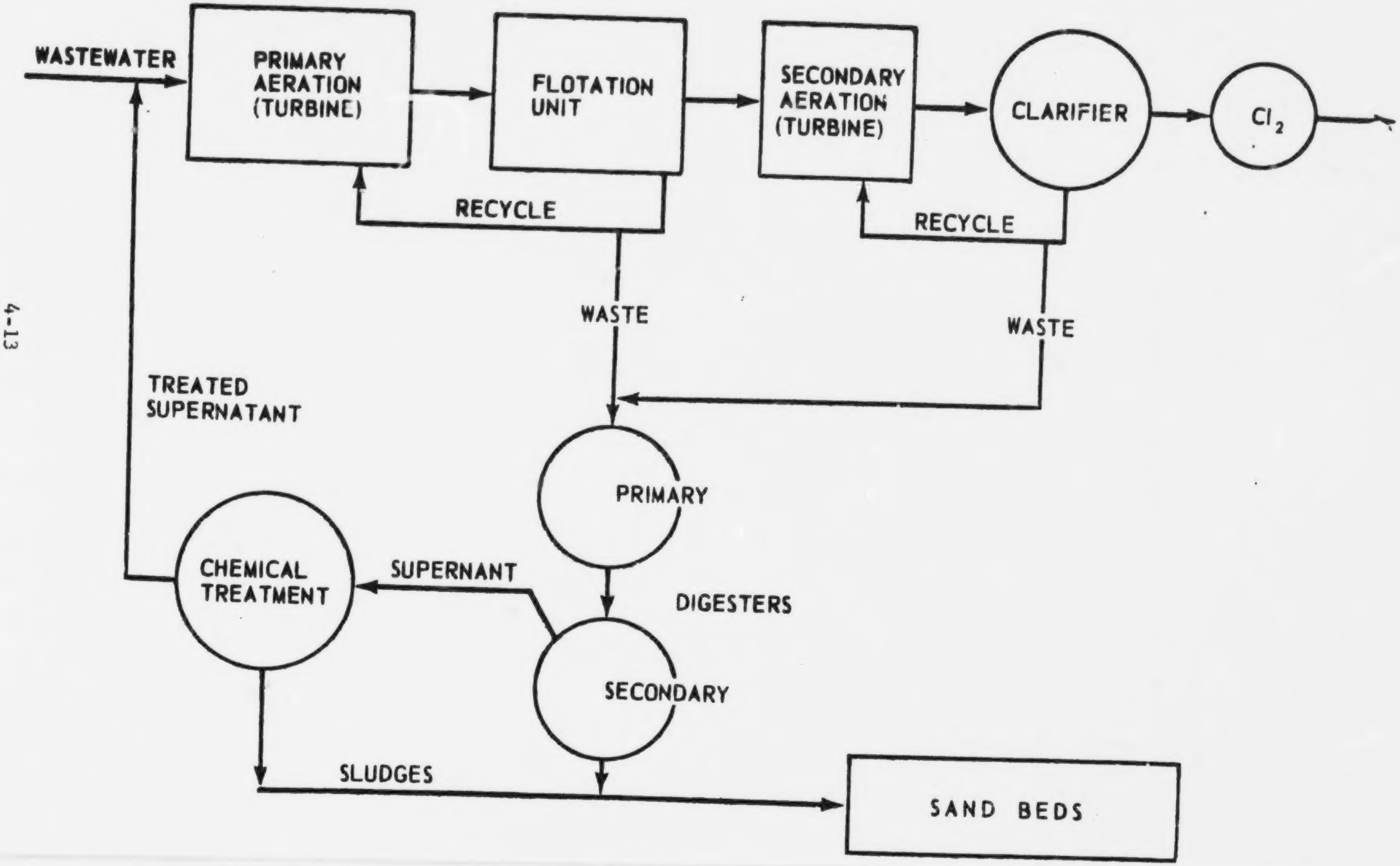

WASTEWATER
PRIMARY AERATION (TURBINE)
FLOTATION UNIT
SECONDARY AERATION (TURBINE)
CLARIFIER
Cl_2
RECYCLE
RECYCLE
WASTE
WASTE
TREATED SUPERNATANT
PRIMARY
DIGESTERS
SECONDARY
CHEMICAL TREATMENT
SUPERNANT
SLUDGES
SAND BEDS

TABLE II

Summary of Supernatant Data (6)

Analysis	80% Confidence	Median	Mean
Bicarbonate Alkalinity (mg/l as $CaCO_3$)	850 - 2,950	1,580	1681
5-Day BOD (mg/l)	500 - 4,260	910	1401
Total Phosphate (mg/l as PO_4)	46 - 380	132	211
(mg/l as P)	15 - 124	43	69
Ammonia Nitrogen (mg/l)	100 - 710	405	413
pH	6.6 - 8.0	7.3	7.3

(6) Masselli, Joseph W. et.al. "The Effect of Industrial Wastes on Sewage Treatment". New England Water Pollution Control Commission, Boston, Massachusetts (1965).

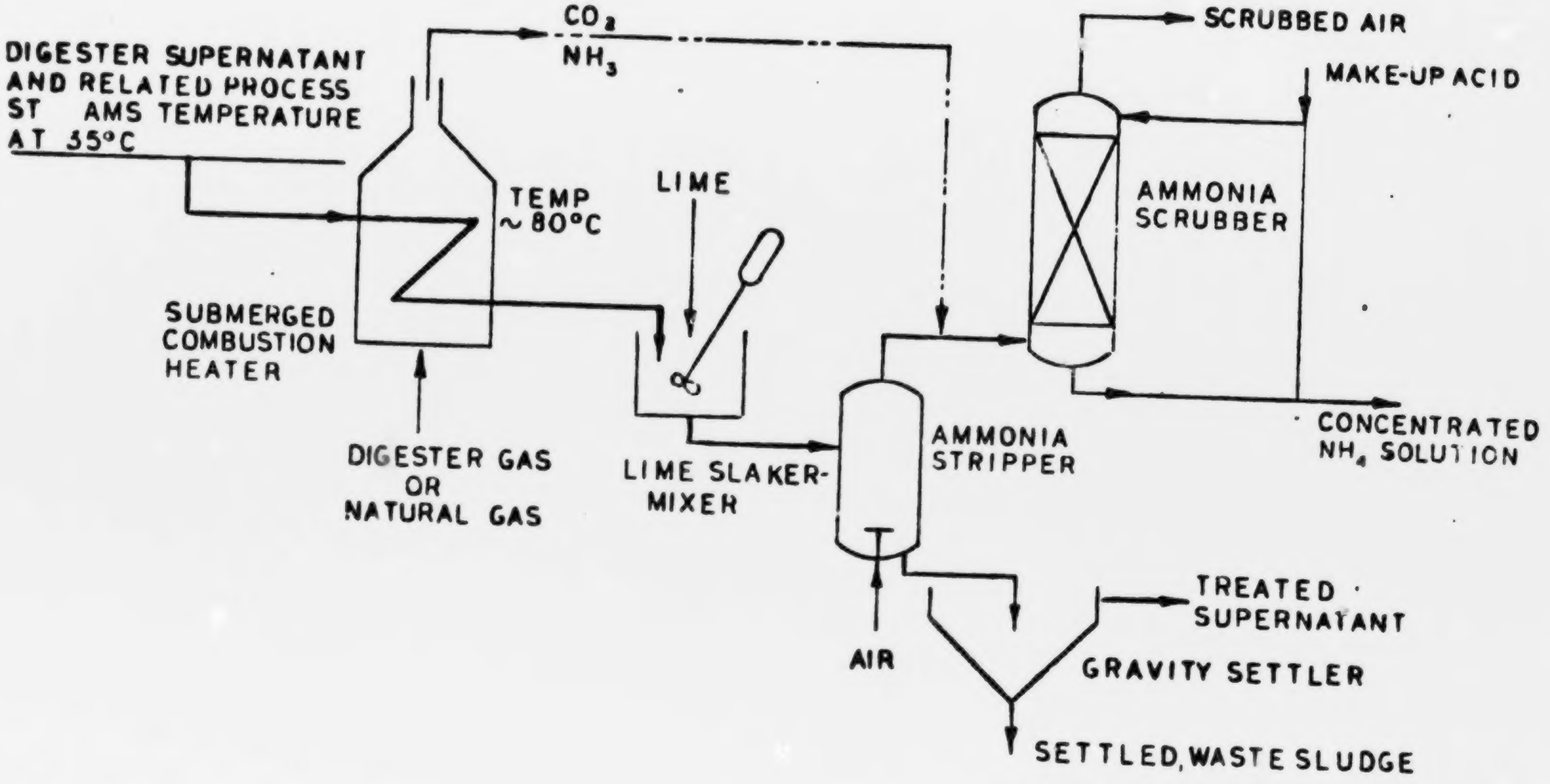

DIGESTER SUPERNATANT AND RELATED PROCESS ST AMS TEMPERATURE AT 35°C
CO_2
NH_3
TEMP ~ 80°C
LIME
SUBMERGED COMBUSTION HEATER
DIGESTER GAS OR NATURAL GAS
LIME SLAKER-MIXER
AMMONIA STRIPPER
AIR
SCRUBBED AIR
MAKE-UP ACID
AMMONIA SCRUBBER
CONCENTRATED NH_4 SOLUTION
TREATED SUPERNATANT
GRAVITY SETTLER
SETTLED, WASTE SLUDGE

FIGURE - 1

FMC CORPORATION
CENTRAL ENGINEERING LABORATORIES

TREATMENT SYSTEM
DIGESTER SUPERNATANT

B

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10. Westberg, N., "Nutrient Salt Reduction at Sewage Treatment Works." Vattenbygien, 19, 2-10 (1963). (In English).

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12. Mulbarger, M. C. and Castelli, J. A., "A Versatile Activated Sludge Pilot Plant," 21st Annual Purdue Industrial Waste Conferences, Purdue University, 1966.

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PHOSPHORUS REMOVAL BY TERTIARY TREATMENT WITH LIME AND ALUM

by

Robert B. Dean
Chief, Ultimate Disposal Research Program
Advanced Waste Treatment Research Laboratory

First Technical Session
11:45 A.M.
Wednesday, February 5, 1969

Symposium on Nutrient Removal and Advanced Waste Treatment
Portland, Oregon

I. LIME TREATMENT OF SECONDARY EFFLUENT

A. Chemistry -- in secondary effluent

1. a. $Ca(OH)_2 + HCO_3^- \longrightarrow CaCO_3 \downarrow + OH^- + H_2O$ (1)

   Slaked lime + alkalinity ⟶ calcium carbonate + hydroxyl ion

   b. $Ca^{++} + HCO_3^- + OH^- \longrightarrow CaCO_3 \downarrow + H_2O$ (2)

   Calcium in water + alkalinity ⟶ calcium carbonate

   c. $5\ Ca^{++} + 4\ OH^- + 3\ HPO_4^= \longrightarrow Ca_5\ OH(PO_4)_3 \downarrow + 3\ H_2O$ (3)

   Orthophosphate ⟶ hydroxyapatite

   d. $Mg^{++} + 2\ OH^- \longrightarrow Mg(OH)_2 \downarrow$ (4)

   Magnesium in water ⟶ magnesium hydroxide

2. a. Equations 1 and 2 are complete above pH 9.5.

   b. Equation 3 forming hydroxyapatite starts above pH 7 but is very slow below pH 9. Hydroxyapatite is the only stable phase in alkaline water.

   c. Some phosphate may be colloidally dispersed as hydroxyapatite and escape sedimentation.

   d. $Mg(OH)_2$ equation is a gelatinous precipitate that collects particles.

   e. Phosphate removal improves as pH is raised.

B. Lime Requirements

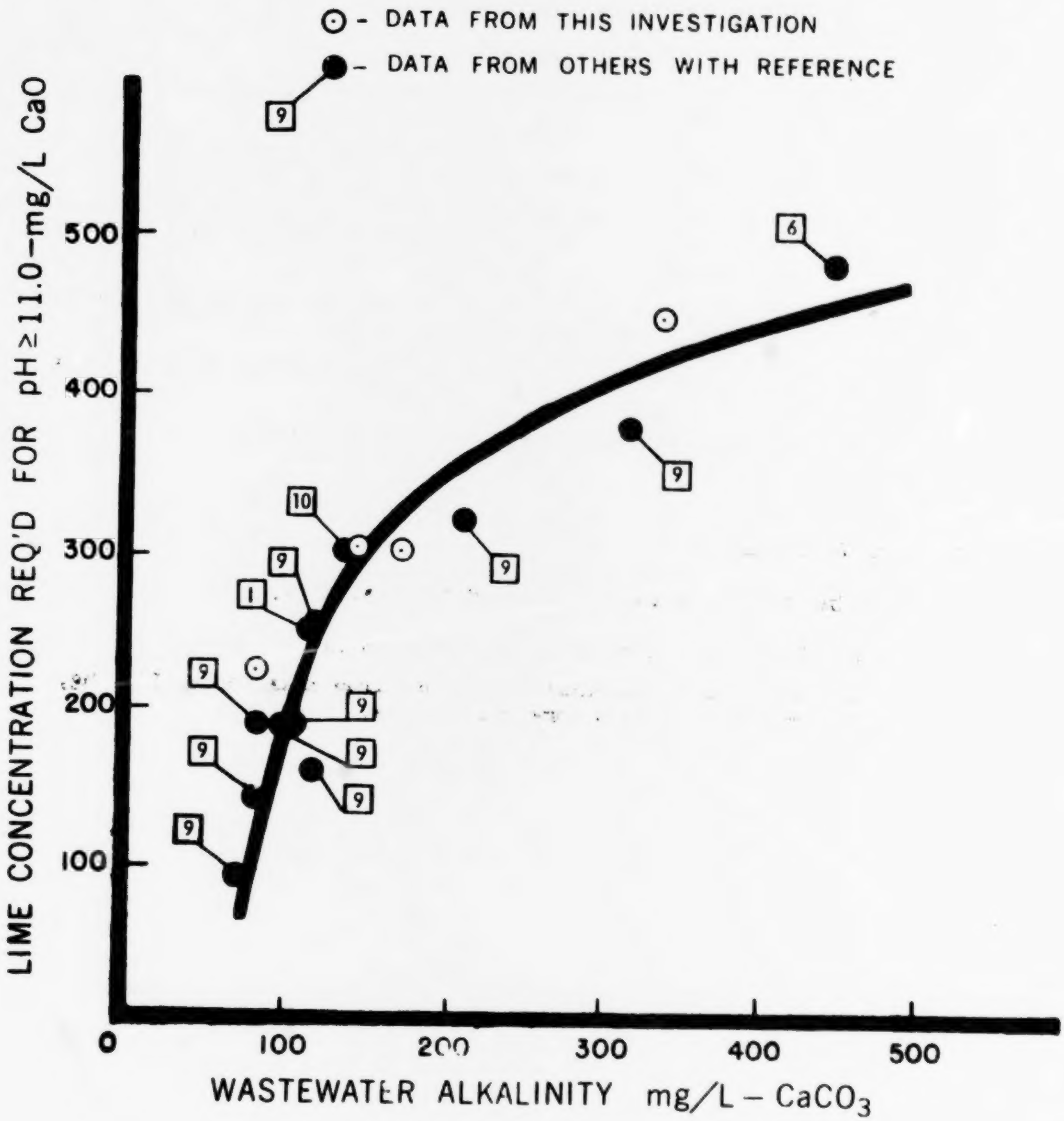
1. Lime dose is primarily related to alkalinity.

   a. Figure 1. Lime as CaO to reach pH 11.

   b. Attempts to calculate lime dose from alkalinity, PO_4, Mg, NH_4, etc. always come out too low.

FIGURE 1

LIME REQUIREMENT FOR pH≥11.0 AS A FUNCTION OF THE WASTEWATER ALKALINITY



C. Systems

1. Single Stage

   a. Add lime slurry to pH 9.5, settle.

   b. Precipitate calcium carbonate, calcium phosphate (hydroxyapatite) and organics.

   c. Calcium phosphate may be difficult to collect. May need coagulant aids. Iron salts, activated silica or polymers and filtration.

2. Two Stage. Figure 2, System A.

   a. Add lime slurry to pH 11+, settle. Recarbonate to pH 9.5. Clarify.

   b. First stage precipitates calcium carbonate, calcium phosphate, magnesium hydroxide and organics.

   c. High pH is suitable for ammonia removal by air stripping.

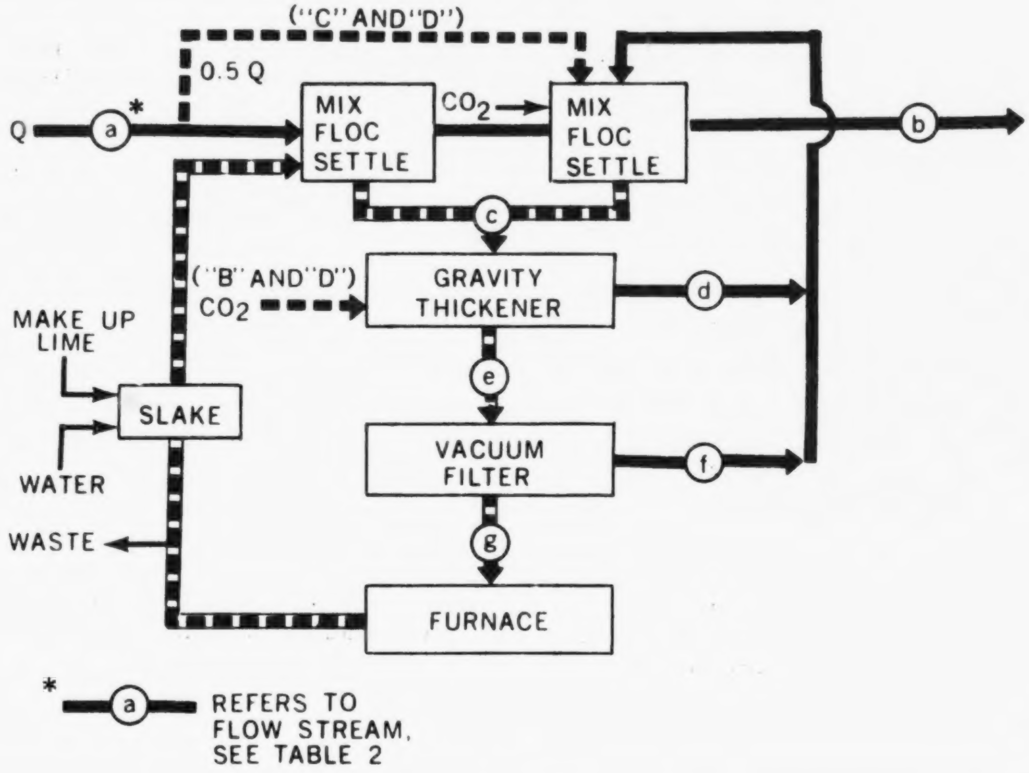
   d. Sludge may be recarbonated with flue gasses to redissolve magnesium hydroxide and aid filtration. Figure 2, Systems B and D.

   e. Second stage precipitates only $CaCO_3$ (100 mg/l) if CO_2 is used.

   f. Split treatment uses alkalinity in part of the stream to adjust pH to 9.5, Systems C and D. Precipitate contains calcium phosphate and some organics as well as calcium carbonate.

FIGURE 2

EXPERIMENTAL SYSTEMS


("C" AND "D")
0.5 Q
Q
a
*
MIX FLOC SETTLE
CO_2
MIX FLOC SETTLE
b
c
("B" AND "D")
CO_2
GRAVITY THICKENER
d
MAKE UP LIME
SLAKE
WATER
e
VACUUM FILTER
f
WASTE
g
FURNACE
* a REFERS TO FLOW STREAM, SEE TABLE 2

SYSTEM "A"
TOTAL TREATMENT

SYSTEM "B"
TOTAL TREATMENT WITH SLUDGE CARBONATION

SYSTEM "C"
SPLIT TREATMENT (0.5Q to 2nd STAGE)

SYSTEM "D"
SPLIT TREATMENT WITH SLUDGE CARBONATION

NOTE: LIME DOSE FOR SYSTEMS "C" AND "D" IS ½ OF THE LIME DOSE USED FOR SYSTEMS "A" AND "B"

D. quipment

1. Slake lime as CaO in slurry or paste slaker to make a slurry of $Ca(OH)_2$ in saturated water.
2. Rapid mix tank or zone for precipitation.
3. Clarifier to remove solids.
    - a. Circular. South Lake Tahoe, California. Tables 1 and 2.
4. Sludge blanket systems precipitates in presence of preformed solids.
    - a. Lebanon, Ohio. Figure 3. 75 gpm.
    - b. Upflow rate 1 gpm/ft^2, 110 minutes detention.
    - c. Sludge sucked up from bottom, mixed with new lime and secondary effluent.
    - d. Water rises through sludge blanket. Top of blanket is organic and colloidal, larger calcium carbonate settles out.
    - e. Remove sludge as 2-3% slurry and gravity thicken to 10%.
    - f. Poor performance when biological plant is upset and high colloids are coming over.
    - g. Coagulant aids not needed during normal operation.
5. Lime Solution System
    - a. Requires high volume ratio of lime water to effluent. About 1/4 of total flow.
    - b. Does not recycle insolubles from recovered lime.
6. Filters to remove residual turbidity and colloidal phosphates.
    - a. Multi-media -- coal on sand, etc., or rapid sand filter.
    - b. Effluent needs pH adjustment to avoid calcium carbonate precipitation on media.

PROCESS EQUIPMENT

Primary and Secondary Treatment. Process equipment used at this plant for primary and secondary treatment is quite conventional in design and design loadings for various units may be termed conventional. Both rectangular and circular primary clarifiers are employed; each exhibit approximately equal efficiencies. Both conventional spiral roll and completely mixed activated sludge systems are used; oxygen transfer to the spiral roll system is by means of coarse bubble diffused air and to the completely mixed system by means of sparged turbine aerators. As expected, the completely mixed activated sludge system exhibits much more stable operation and load handling ability than does the spiral roll system. Two types of circular, sludge suction type, secondary clarifiers are employed. Performance data from these secondary clarifiers to date does not indicate significant difference in the efficiency or performance of the two units.

Wasting of activated sludge is accomplished by means of a mass density system which provides automated control of sludge wasting. The system employs a nuclear density meter to determine percent solids contained in the waste sludge. Waste sludge flow is measured by a magnetic flow meter. The combined outputs of the density meter and the flow meter are electrically multiplied in an indicator-totalizer and used to position the waste sludge valve by comparison of the multiplied output signal with a preselected wasting rate. Waste sludge is thus recorded in terms of the pounds of dry solids wasted per day (kg/day).

Waste sludge is thickened by means of a flotation type thickener. Polymers are added to enhance thickening and solids capture. Operation of the thickener has been very successful with essentially 100 percent solids capture and float production containing 5 percent solids easily obtained. Polymer costs in the range of 3 to 5 dollars per ton ($3.30 to $5.50/metric ton) are normal. Cationic polymers appear most effective with this sludge.

Chemical Coagulation. Chemical coagulation and phosphate removal equipment are also conventional with flash mix, slow mix (flocculation) and a conventional clarifier being employed. Lime dosage to the flash mix is on the order of 400 mg/l as CaO. The addition of approximately 0.25 mg/l polyelectrolyte after flocculation has proven to be very beneficial in reducing effluent turbidity from the clarifier. Turbidity in the chemical clarifier effluent commonly ranges 3 SJU or less. Operating expense to date indicates that conventional clarifiers rather than upflow type mechanisims are definitely preferable for this type of service.

Coagulant Recovery. Spent lime sludge is removed from the clarifier by pumping, thickened in a conventional gravity thickener, dewatered by centrifuge and recalcined for reuse by means of a multiple hearth furnace. Pneumatic conveying equipment is utilized for transporting both recalcined and new lime to overhead storage bins. Gravimetric lime feeders and pug mill type slakers are used to feed $Ca(OH)_2$ slurry to the flash mix bases and other process application points. Lime feed rates are controlled by signal from continuous pH measurement.

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TABLE 1

MAJOR DESIGN CRITERIA FOR THE SOUTH TAHOE PUD WATER RECLAMATION PLANT

Parameter	Design Criteria
Flow	7.5 mgd
BOD conc.	350 mg/l
BOD amount	22,000 lbs/day
SS conc.	200 mg/l
SS amount	12,500 lbs/day
Lime dosage as CaO	400 mg/l
Recalciner capacity	39,600 lbs/day dry solids
Sludge incinerator capacity	21,600 lbs/day dry solids
Carbon furnace capacity	5,000 lbs/day dry spent carbon

Note mgd x 3785 = cu m/day
lbs/day x 0.454 = kg/day

TABLE 2

CHEMICAL AND PHYSICAL CHARACTERISTICS RAW SEWAGE AT SOUTH LAKE TAHOE PUD

Waste Characteristic	Concentration in Raw Sewage
COD	400 - 600 mg/l
Turbidity	High 100 SJU
Phosphate as P	10 - 15 mg/l
Nitrogen	
Organic N as N	10 - 15 mg/l
Ammonia N as N	25 - 35 mg/l
NO_2 and NO_3 as N	Trace

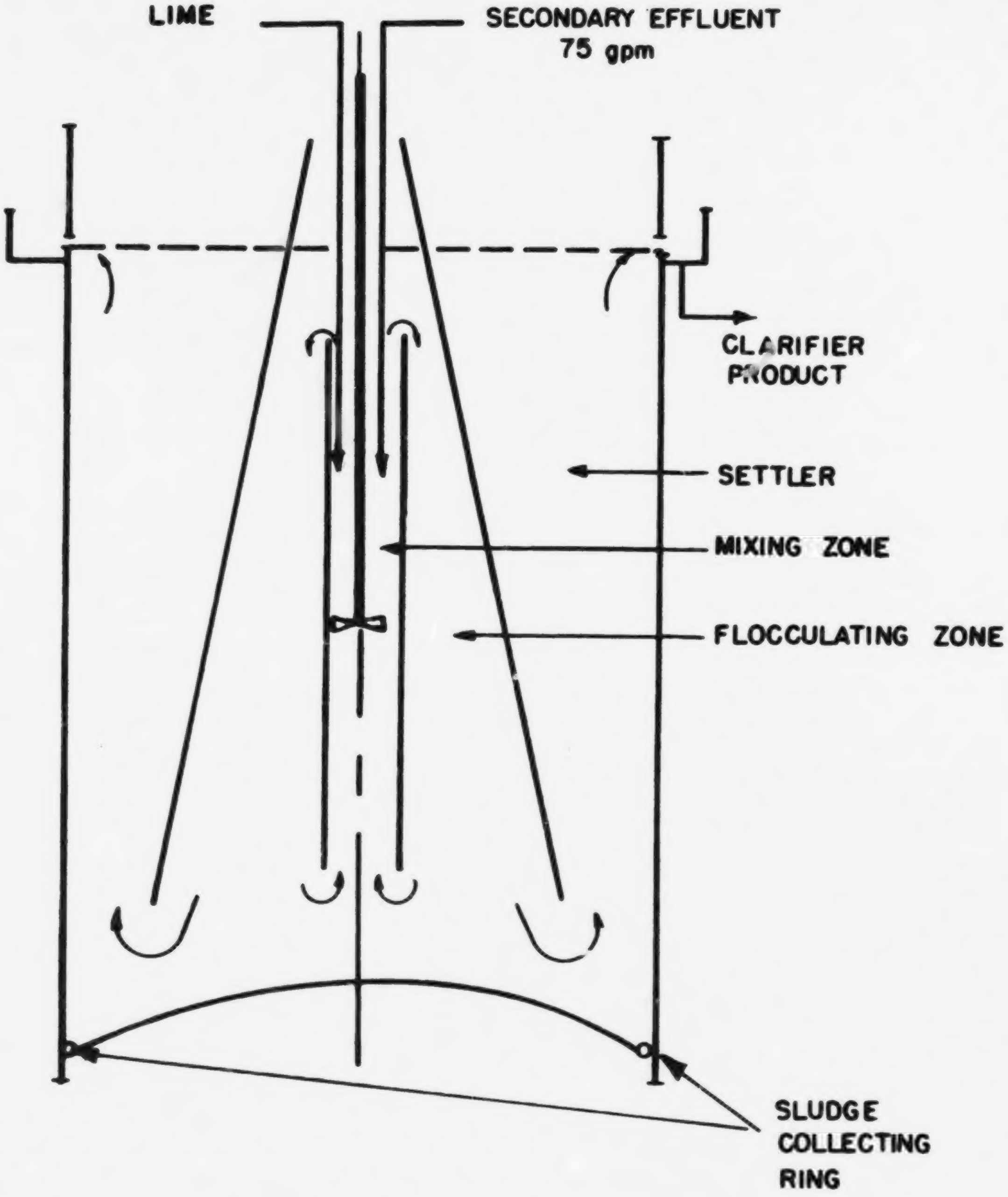
LIME
SECONDARY EFFLUENT
75 gpm
CLARIFIER
PRODUCT
SETTLER
MIXING ZONE
FLOCCULATING ZONE
SLUDGE
COLLECTING
RING

FIGURE 3. LIME CLARIFIER

E. Performance

1. Single Stage Clarifier (Lebanon). Figure 4.

   a. Effluent:

Ca	100 mg/l
Mg	30 mg/l
$PO_4 \cdot P$	10 mg/l
Alkalinity	400 mg/l

   b. 90% removal above pH 9.7

2. Single Stage plus Dual Media Filters. Figure 5.

   a. Media. 18" - 0.75mm anthracite
      6" - 0.46mm sand

   b. Operation. 2 gpm/ft^2 to 7" Hg pressure loss in 48 hours.

   c. 97% Removal of PO_4 at pH 10, 80% at pH 9.0.

   d. Approximately 250 mg/l of $Ca(OH)_2$ (190 mg/l as CaO) required for 80% removal.

3. Two stage.

   a. Tahoe

FINAL EFFLUENT QUALITY

South Lake Tahoe
September 1968

	Median	Maximum
MBAS	0.14	0.19
COD	9.	13.
Turbidity-JU	0.1	0.4
Phosphate-P	0.11	0.17
Nitrogen-N $NH_3 + NO_3^-$	11.4	13.1

   b. Rapid mix before polymer addition.

   c. Recarbonate to pH 7.5.

   d. 110 mg/l fresh lime and 227 mg/l recalcined lime (CaO). Predicted 400 mg/l in lab studies (Slechta '67, Suhr '68)

   e. Washington, D.C. 70 gpm. 90% in clarifier, 95% plus filter. Whole plant, 97%.

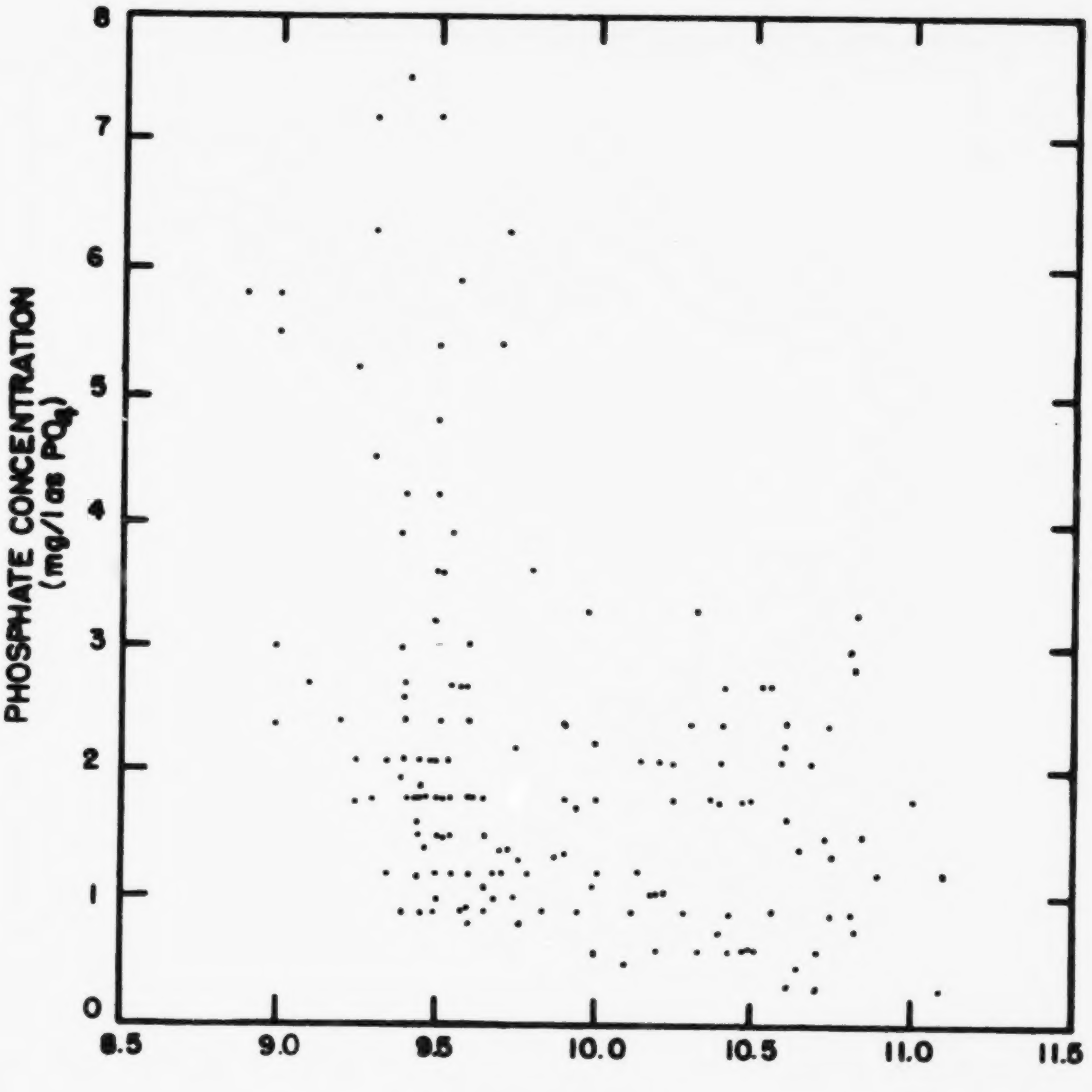

FIGURE 4. EFFECT OF pH ON PHOSPHATE CONCENTRATION OF EFFLUENT FROM LIME CLARIFIER

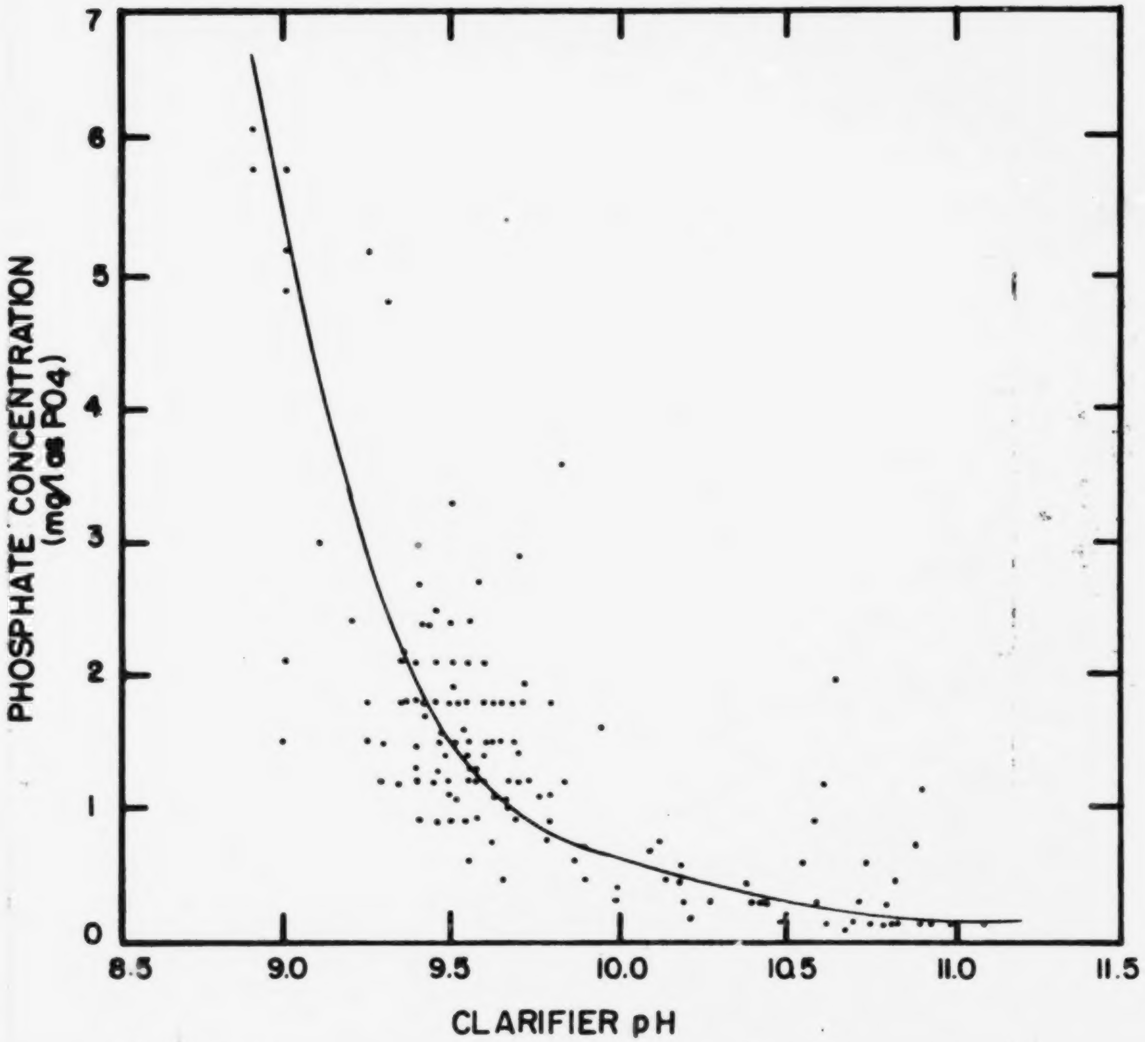

FIGURE 5. EFFECT OF pH ON PHOSPHATE CONCENTRATION OF EFFLUENT FROM FILTERS FOLLOWING LIME CLARIFIER

4. Lime Recovery Studies. Two Stage, 75 l batch (Mulbarger). Figure 2.
    a. Hard water (340 mg/l) and relatively soft water (175 mg/l as $CaCO_3$)
    b. Composition did not affect removal efficiencies. 97% SS, 99% PO_4 removal.
    c. Split treatment reduced PO_4 removal to 90%.

F. Cost of Lime Treatment
    1. Without recarbonation or post filtration. Table III
        a. 300 mg/l $Ca(OH)_2$ (225 mg/l CaO)
        b. 0.87¢/1000 gal. for coagulant aid equivalent to 50 mg/l $FeSO_4$.
        c. 4-1/2% for 25 years.
        d. Cost of recalcined lime is close to cost of fresh lime.
        e. Savings are in reduced disposal of lime sludge.
    2. Lake Tahoe. 7.5 mgd plant (4.5 mgd operation)
        a. 9¢/1000 gal. (Suhr) versus 10.4 estimated (Slechta). Lime costs $24.50/ton because of high freights.

TABLE III

TOTAL COST OF PHOSPHATE REMOVAL (Cents per 1000 gallons)	Size of Plant			
	1 mgd	10 mgd	100 mgd	250 mgd
Capital amortization	.97	.79	.65	.59
Land amortization	.09	.09	.09	.09
Operating and maintenance	.41	.14	.08	.06
Cost of chemicals				
Lime	1.75	1.75	1.75	1.75
Iron salt	.87	.87	.87	.87
Cost of sludge disposal by hauling (to land fill (25-mile one-way trip)	.67	.67	.67	.67
TOTAL	4.76	4.31	4.11	4.03
Savings if sludge can be recalcined	-.67	-.67	-.67	-.67
TOTAL (with recalcining)	4.09	3.64	3.44	3.36

Source: FWPCA, Lake Michigan Water Pollution Enforcement Conference

II. TREATMENT OF SECONDARY EFFLUENT WITH ALUMINUM IONS

A. Chemistry

1. Low pH. Alum. $Al_2(SO_4)_3 \cdot X\ H_2O \longrightarrow Al^{+++}$
    a. $Al^{+++} + H_2PO_4^- \longrightarrow Al\ PO_4 + 2\ H^+$
2. Above pH 5-6 also get aluminum hydroxide precipitation
    a. $Al^{+++} + 3\ OH^- \rightleftarrows Al(OH)_3 \downarrow$ and

       $Al(OH)_3 + H\ PO_4^{=} \longrightarrow Al \cdot PO_4 + 2\ OH^- + H_2O$
    b. Final product approximates $Al(OH)_3 \cdot Al\ PO_4$,

       but mole ratio depends on pH. Figures 9 and 10.
    c. Aluminate is an alternative source of aluminum hydroxide.

       $Al(OH)_4^- + H^+ \longrightarrow Al(OH)_3 \downarrow + H_2O$
    d. Natural alkalinity can supply H^+ or OH^- within limits.

       $3\ HCO_3^- + Al^{+++} + 3\ H_2O \longrightarrow Al(OH)_3 + 3\ H_2CO_3$

       $HCO_3^- + Al(OH)_4^- \longrightarrow Al(OH)_3 + CO_3^{=} + H_2O$
    e. Alum and aluminate can be combined:

       $Al^{+++} + 3\ Al(OH)_4^- \longrightarrow 4\ Al(OH)_3$
    f. Polyphosphates are harder to remove than ortho (Stumm) and may reduce removal percentage.

B. Dose Requirements

1. Basic requirement 2 Al to 1 P.
    a. Substantially greater than for clarification. Figure 7.
    b. At Lebanon: 250 mg/l alum for 90% removal
       At Tahoe (Slechta): 300 mg/l for 90% removal

C. Systems and Equipment

1. Similar to Lime
2. Lower rise rates in clarifier 0.5 - 0.75 mg/l.
3. Post filtration needed only to exceed 80% removal.
4. Sludge Disposal is a major unsolved problem.

D. Performance

1. Lebanon. Table 3 and Table 4.
    a. 90% removal of PO_4 without filtration using activated silica as a coagulant aid.
    b. Filtration increased P removal to 96% and significantly improved solids removal.

E. Costs

1. 10 mgd plant requiring 300 mg/l alum plus 2.5 mg/l silica.
    a. Clarifier only. 80-90% removal of P. Cost 3.9¢/1000 gal.
    b. Filter after Clarifier. 96% removal of P. Cost 7.4¢/1000 gal.
2. Does not include sludge disposal.
    a. Freezing especially natural.
    b. Aluminate recovery. See later papers.

TABLE 1. OPTIMUM OPERATING CONDITIONS FOR TERTIARY CLARIFICATION USING ALUM COAGULATION FILTRATION AT LEBANON, OHIO

Variable	Range	Optimum Value
(1) Overflow Rate GPD/FT^2	300-900	700[1.]
(2) Alum Dose mg/l		
(a) Clarification	0-500	150
(b) Phosphate removal	0-500	300
(3) Type of Media		(c) Sand and coal dual media
(a) Sand		
(b) Coal		
(c) Sand and coal		
(4) Effective Size of Coal mm.	0.75-1.80	1.4 @ 4 GPM/FT^2
Sand Size 0.45 mm.		1.3 @ 3 GPM/FT^2
(5) Filtration Rate GPM/FT^2	2-5	4
(6) Floc Strengtheners		
(a) Activated silica	0.15 mg/l	3 mg/l
(b) Cationic polyelectrolyte C-7*	0-1.5	1.5 mg/l
(7) Source of AL^{+++} on Phosphate Removal		
(a) Alum	0-100%	No difference until pH exceeded 8.0. This occurred when 90% of AL^{+++} came from the aluminate
(b) Aluminate	0-100%	
(c) Both		

*A product of Robin and Haas Company, Philadelphia, Pa.

1. 700 GPD/FT^2 based on economic considerations; optimum solids removal efficiency occurred at the 300 GPD/FT^2 rate.

TABLE 2. TYPICAL RESULTS UNDER OPTIMUM OPERATING CONDITIONS

Process Stream	Suspended Solids, mg/l	Acid Hydrolyzable Phosphate, mg/l $PO_4^{\equiv}$	Turbidity J.T.U.
Secondary Effluent	45.6	22.4	12.2
Chemically Treated Settled Effluent	11.0(76%)*	2.2(90%)	1.5(88%)
Filtered Product	1.3(97%)	0.9(96%)	0.5(96%)

Operating Conditions:

Overflow Rate: 700 GPD/FT^2
Alum Dose: 82 mg/l
Aluminate Dose: 68 mg/l
Silica Dose: 3 mg/l

Filtration Rate: 3GPM/FT^2
Effective Size of Coal: 1.325 mm
Length of Run: 25 hours
Sludge Concentration: 1.2% by weight
Solids Concentration in Filter Backwash Water: 475 mg/l

* Denotes Removal Efficiency as %

The clarifier is operated at a rise rate of 1 gpm/ft^2. Dual media filters; consisting of 18 inches of 0.75 mm coal over 6 inches of 0.45 mm sand polish the clarifier effluent. The filters are operated at 2 gpm/ft^2 to a terminal headloss of 9 feet of water. Some preliminary operating results are shown in Table 3.

The suspended solids concentration of the settled sludge ranged from 1.5 to 2.5% solids by weight and was further concentrated to 12-15% solids by weight in a gravity thickener and additional drying on sand beds prior to disposal to a land fill.

C Jar Test Results

When effluent quality standards require the removal by phosphate in addition to clarification, significantly higher coagulant doses can be anticipated. A rough stoichiometry of 2 moles of AL^{+++} to 1 mole of P has been found empirically, to exist in tertiary treatment applications.

In addition, as shown in Figure 1 all the primary coagulants are equally effective in removing phosphate. These results were obtained from jar test studies[11] on a pilot plant activated sludge effluent.

VI INDUSTRIAL APPLICATIONS[12]

A Food Industry

1 Meat

Grit removal, flocculation and sedimentation will remove 50% of the total volatile solids and BOD and 75% of the suspended solids in a manure-bearing wastewater. Alum coagulation removes an additional 2.5 mg/l of BOD and 1.5 mg/l of grease per mg/l of alum added. The chemical costs for 50% and 78.5% increased removal efficiency is \$0.64 to \$2.05 per 100 lb. BOD removal, respectively.

2 Poultry process wastes

Plain sedimentation can remove 17-28% of the BOD and 30-65% of the S.S.

TABLE 4. TYPICAL RESULTS UNDER OPTIMUM OPERATING CONDITIONS

Process Stream	Suspended Solids, mg/l	Acid Hydrolyzable Phosphate, mg/l $PO_4^{\equiv}$	Turbidity J.T.U.
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* Denotes Removal Efficiency as %

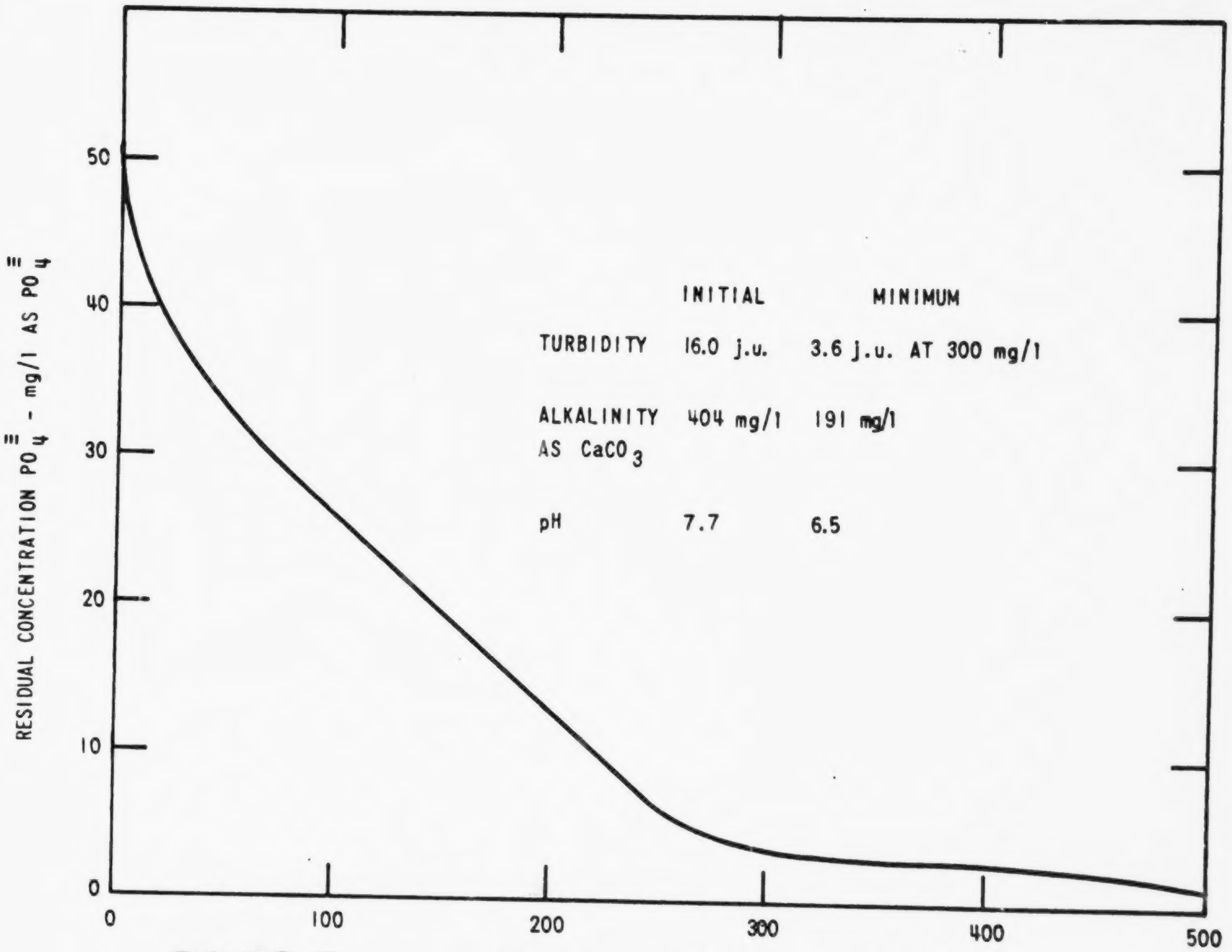

FIGURE 7

EFFECT OF ALUM ADDITION ON PHOSPHATE REMOVAL.

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PHOSPHORUS REMOVAL
BY
MINERAL ADDITION

E. F. Barth

ADVANCED WASTE TREATMENT SEMINAR

Portland, Oregon

February 5 and 6, 1969

PHOSPHORUS REMOVAL BY MINERAL ADDITION

Portland, Oregon
February 5 and 6, 1969

The combined chemical-biological approach to phosphorus removal offers several advantages.

Screening data shows that effluent phosphorus concentrations are related to the cations present in the wastewater.

Various flow patterns are used in the mineral addition process. Results from dosing a 2 mgd activated sludge plant will be presented. Comparison of alum versus aluminate and observed operational problems will be discussed.

Logistics of mineral addition versus tertiary coagulation will be considered.

The results of dosing aluminum compounds directly onto trickling filter rocks will be shown.

Brief mention will be made of straight chemical processes for phosphorus control of effluents along with a listing of advanced processes under development.

The following slides will be used and, where available, a reproduction of the slide is attached:

Slide No.	Title
1	Advantages of Direct Addition
2	Screening Data
3	Flow Diagram of Chemical-Biological Processes
4	Flow Diagram of Pomona Plant

5 View of Chemical Dosing at Pomona
6 Aeration Chamber - Pomona
7 Final Data - Pomona
8 Alum Versus Aluminate
9 pH and Turbidity
10 Mineral Addition Versus Tertiary Coagulation
11 Fairborn Plant
12 Chemical Dosing - Fairborn
13 Chemical Pump - Fairborn
14 Dosing at Weir Crest
15 Filter Spray
16 Pilot Settler
17 Final Effluent - Fairborn
18 Results - Fairborn
19 Straight Chemical Approaches
20 Advanced Processes

COMBINED BIOLOGICAL AND CHEMICAL PROCESSES

Add Mineral Supplement Directly to Aerator

I. Dual Use of Aerator
  a) Mixing by Diffusion Apparatus
  b) Residence Time for Reactions

II. Tremendous Surface Area of Floc Available

III. Uses Existing Final Settler

TABLE II

Results of Screening for Mineral Supplement
to Activated Sludge Process
Direct Dosage to Aerator
No Supernatant Recycle, No Primary Settling

Mineral Addition	Introduced as	To Form	Overall Removal
None (base line)	-	-	40%
Ca, 150 mg/l	CaO	Hydroxyapatite	64%
Ca, 150 mg/l plus F, 6 mg/l	CaO NaF	Apatite	75%
Mg, 20 mg/l	$MgSO_4$	$MgNH_4PO_4$	50%
Fe, 15 mg/l	$FeCl_3$	$FePO_4$	75%*
Al, 20 mg/l	$Al_2(SO_4)_3$	$AlPO_4$	70%*
Al, 30 mg/l plus Ca, 20 mg/l	$Al_2(SO_4)_3$ CaO	$AlPO_4$	90%

* Turbid effluents

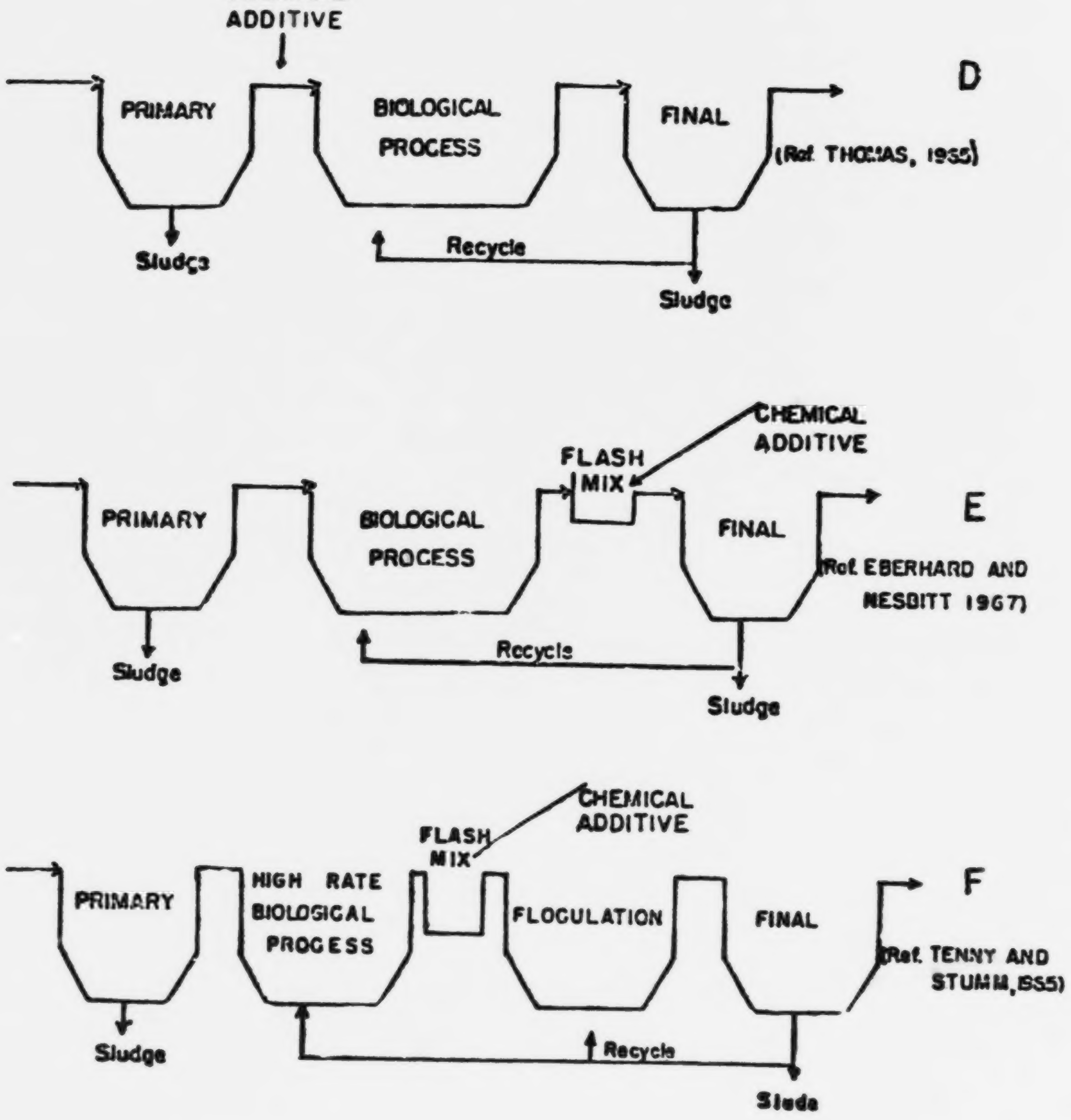

CHEMICAL ADDITIVE
PRIMARY
BIOLOGICAL PROCESS
FINAL
D
(Ref. THOMAS, 1955)
Sludge
Recycle
Sludge
CHEMICAL ADDITIVE
FLASH MIX
PRIMARY
BIOLOGICAL PROCESS
FINAL
E
(Ref. EBERHARD AND NESBITT 1967)
Sludge
Recycle
Sludge
CHEMICAL ADDITIVE
FLASH MIX
PRIMARY
HIGH RATE BIOLOGICAL PROCESS
FLOCULATION
FINAL
F
(Ref. TENNY AND STUMM, 1955)
Sludge
Recycle
Sludge

FIGURE 3. COMBINED CHEMICAL- BIOLOGICAL, VARIATIONS OF BASIC SYSTEMS

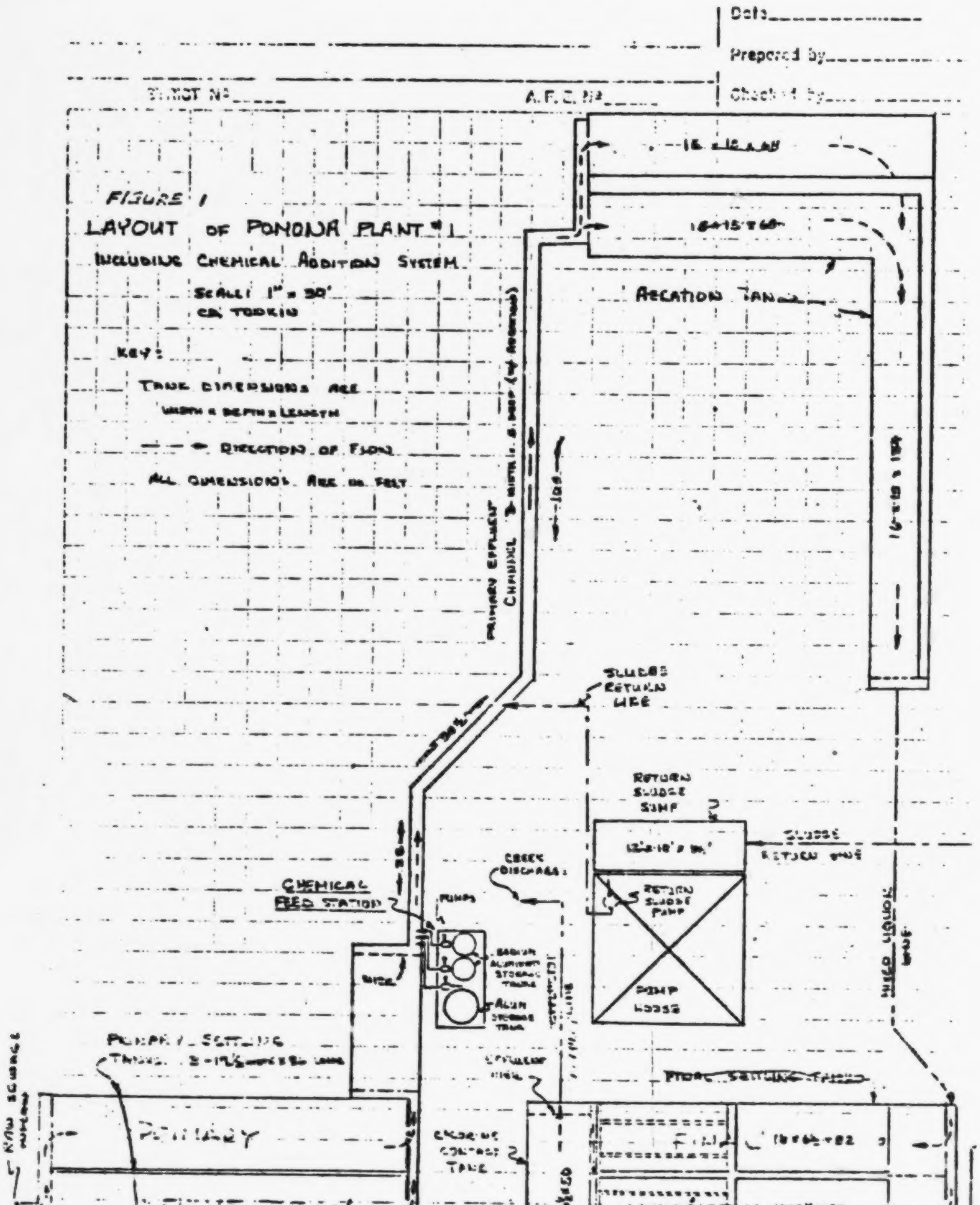


FIGURE 1

LAYOUT OF POMONA PLANT #1

INCLUDING CHEMICAL ADDITION SYSTEM

SCALE: 1" = 30'

Date
Prepared by
Checked by
A.F.E. No.
KEY:
TANK DIMENSIONS ARE WIDTH x DEPTH x LENGTH
DIRECTION OF FLOW
ALL DIMENSIONS ARE IN FEET
AERATION TANK
PRIMARY EFFLUENT CHANNEL
SLUDGE RETURN LINE
RETURN SLUDGE SUMP
RETURN SLUDGE PUMP
PUMP HOUSE
SLUDGE RETURN LINE
MIXED LIQUOR LINE
CREEK DISCHARGE
CHEMICAL FEED STATION
PUMPS
SODIUM ALUMINATE STORAGE TANK
ALUM STORAGE TANK
EFFLUENT LINE
PRIMARY SETTLING TANKS
RAW SEWAGE
PRIMARY
SEDIMENTATION
CHLORINE CONTACT TANK
FINAL SETTLING TANKS
FINAL

TABLE 5 1 SUMMARY OF PHOSPHORUS REMOVAL DURING ALUMINUM ADDITION

E 9	CHEMICAL ADDED	Al:P RATIO (lb/lb)		PRIMARY EFFLUENT PHOSPHORUS (mg/l)		SECONDARY EFFLUENT PHOSPHORUS (UNFILTERED)		SECONDARY EFFLUENT PHOSPHORUS (FILTERED)		PERCENT REMOVAL UNFILTERED		PERCENT REMOVAL FILTERED	
		Ave.	Range	Ave	Range	Ave	Range	Ave.	Range	Ave	Range	Ave.	Range
2/26	Sodium Aluminate	1.00	0.77-1.24	13.2	11.1-15.3	2.62	2.48-2.74	2.07	1.92-2.22	80.4	75.4-82.4	83.0	80.0-85.5
3/11	Sodium Aluminate	1.52	1.35-1.76	13.2	11.7-14.9	2.26	1.67-2.94	0.93	0.78-1.17	83.2	77.3-87.7	93.6	92.4-94.2
4/1	ALUM	1.09	0.96-1.29	12.8	11.6-14.4	2.76	1.96-3.26	2.19	1.64-2.64	78.9	72.6-84.6	83.0	78.4-87.0
4/15	ALUM	1.44	1.14-1.70	13.5	11.9-17.0	1.40	1.04-1.76	0.68	0.45-1.01	90.0	87.3-92.3	95.1	92.7-97.4
4/29	ALUM	1.83	1.63-2.07	13.8	12.9-15.6	1.50	0.83-2.08	0.28	0.20-0.36	89.3	85.8-93.6	98.0	97.3-98.5
5/27	Sodium Aluminate	1.45	1.23-1.67	13.2	12.3-14.4	2.44	1.70-3.26	1.38	0.91-2.25	81.7	75.1-87.3	90.0	82.0-93.8

FIGURE 2: VARIATION OF PHOSPHORUS REMOVAL IN POMONA PLANT NO 1 WITH Al:P RATIO USING ALUM AND SODIUM ALUMINATE AS SOURCES OF ALUMINUM

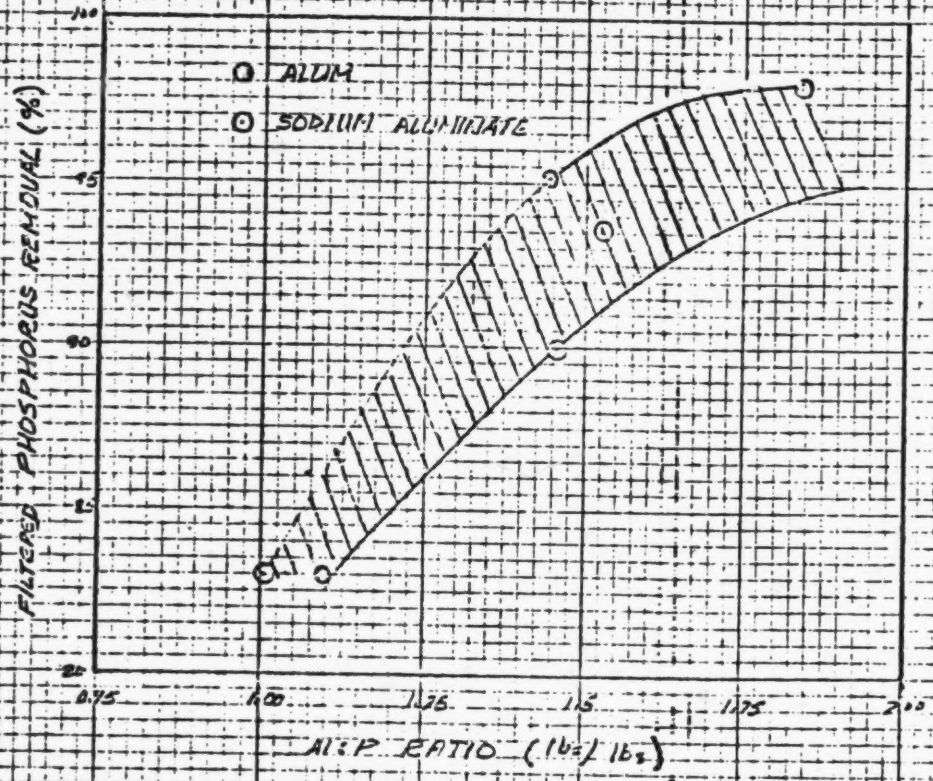
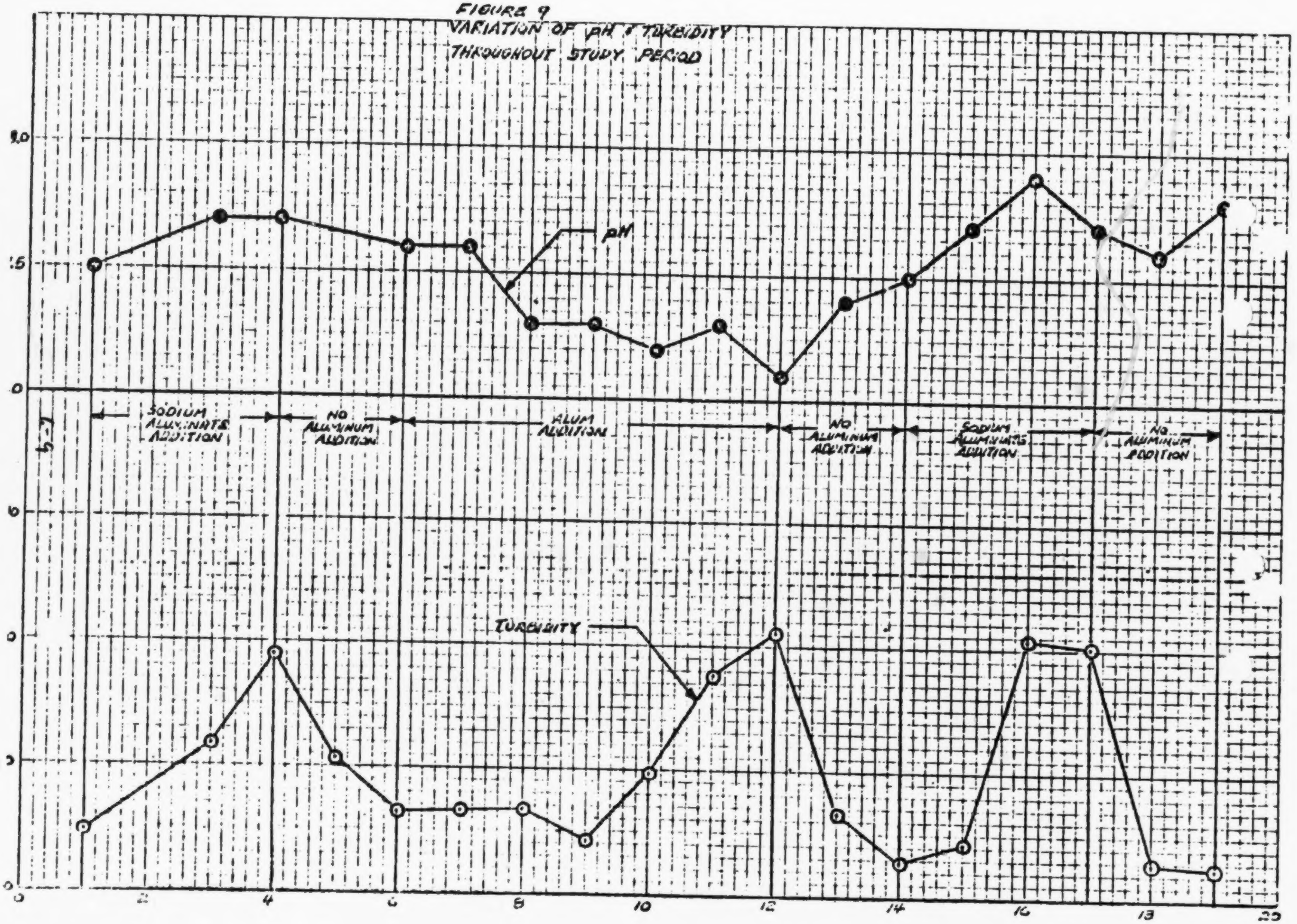
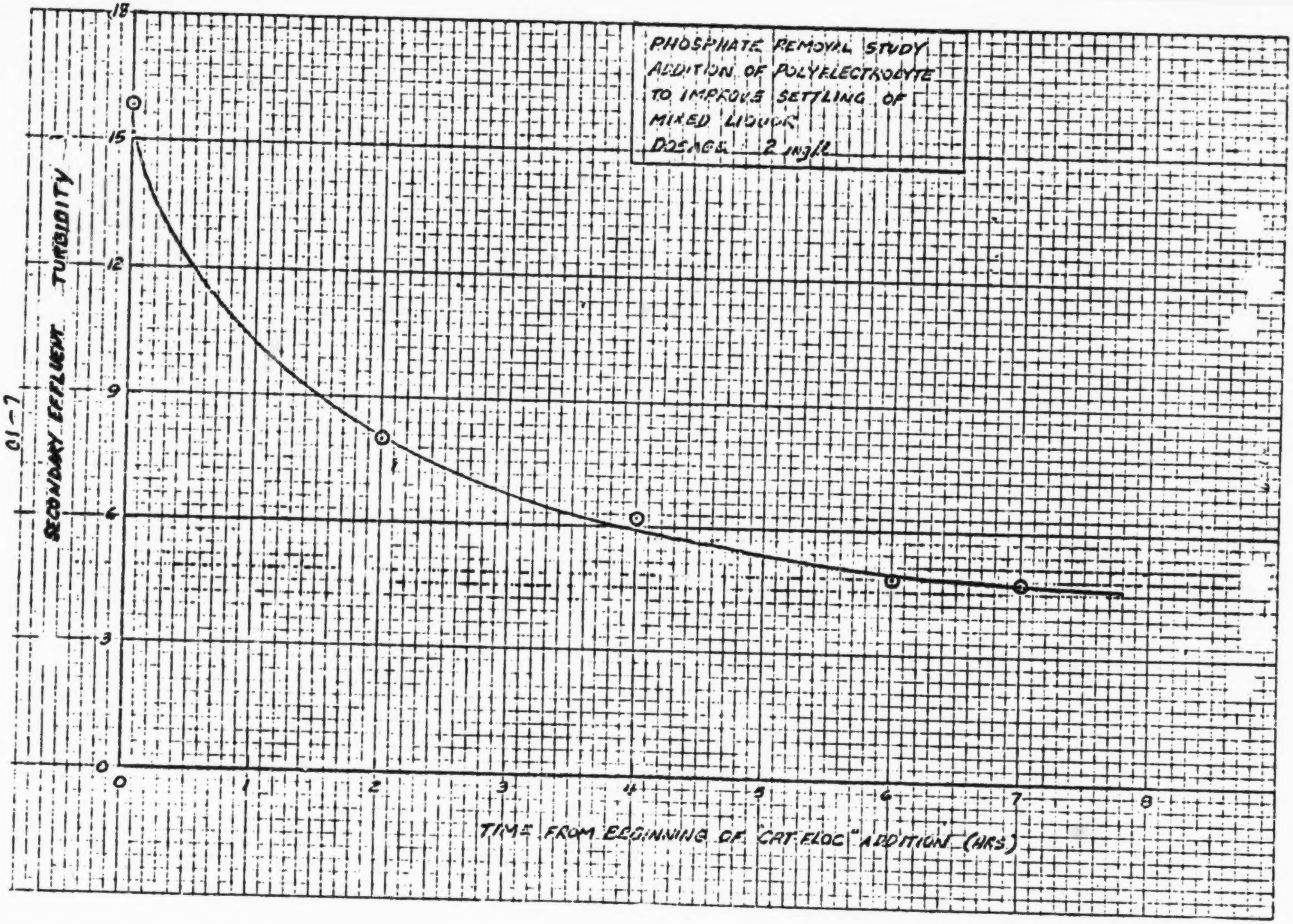
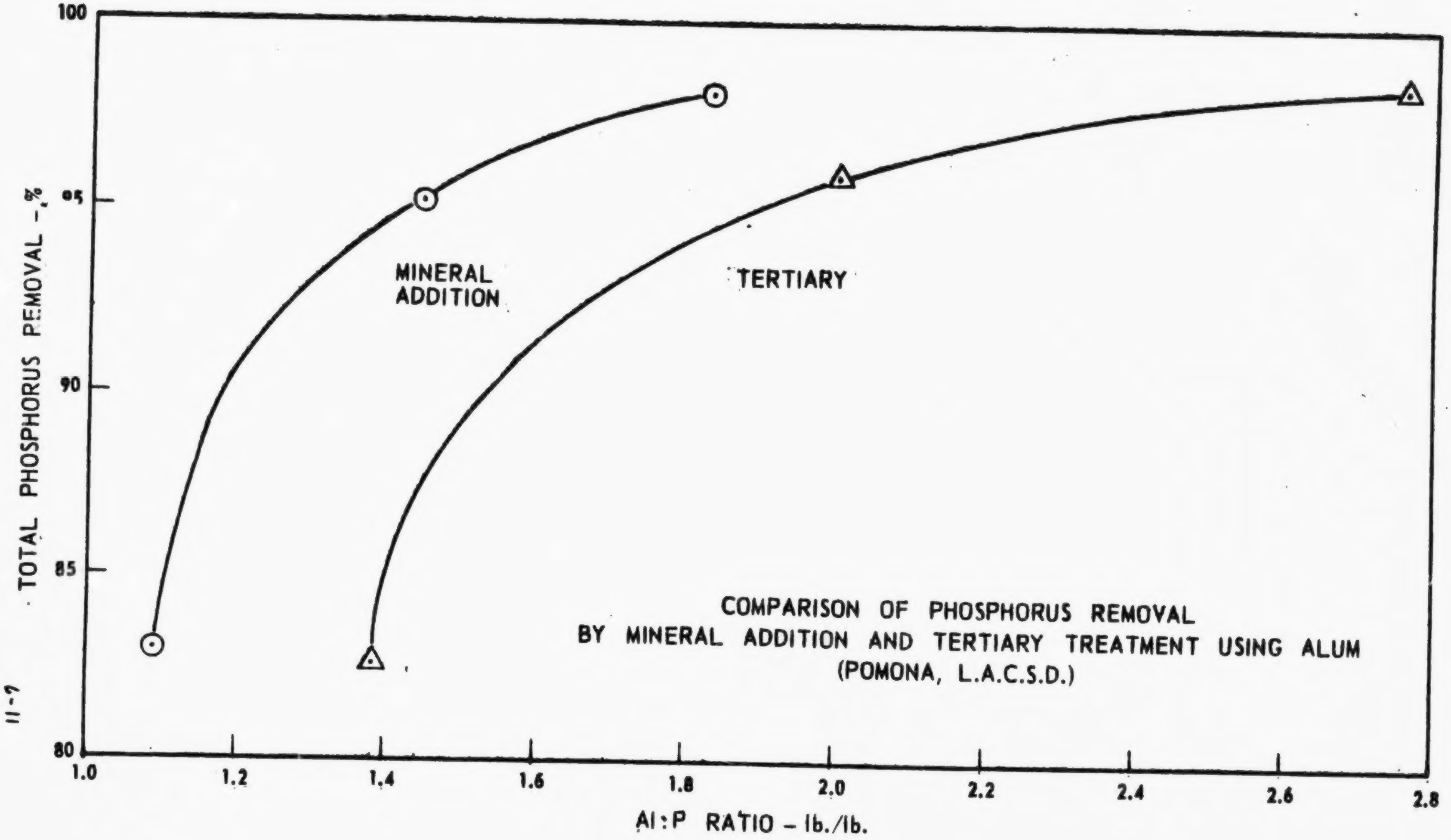


FIGURE 9
VARIATION OF pH & TURBIDITY
THROUGHOUT STUDY PERIOD




PHOSPHATE REMOVAL STUDY
ADDITION OF POLYELECTROLYTE
TO IMPROVE SETTLING OF
MIXED LIQUOR
DOSAGE 2 mg/l
SECONDARY EFFLUENT TURBIDITY
18
15
12
9
6
3
0
0
1
2
3
4
5
6
7
8
TIME FROM BEGINNING OF "CAT-FLOC" ADDITION (HRS)



COMPARISON OF PHOSPHORUS REMOVAL
BY MINERAL ADDITION AND TERTIARY TREATMENT USING ALUM
(POMONA, L.A.C.S.D.)

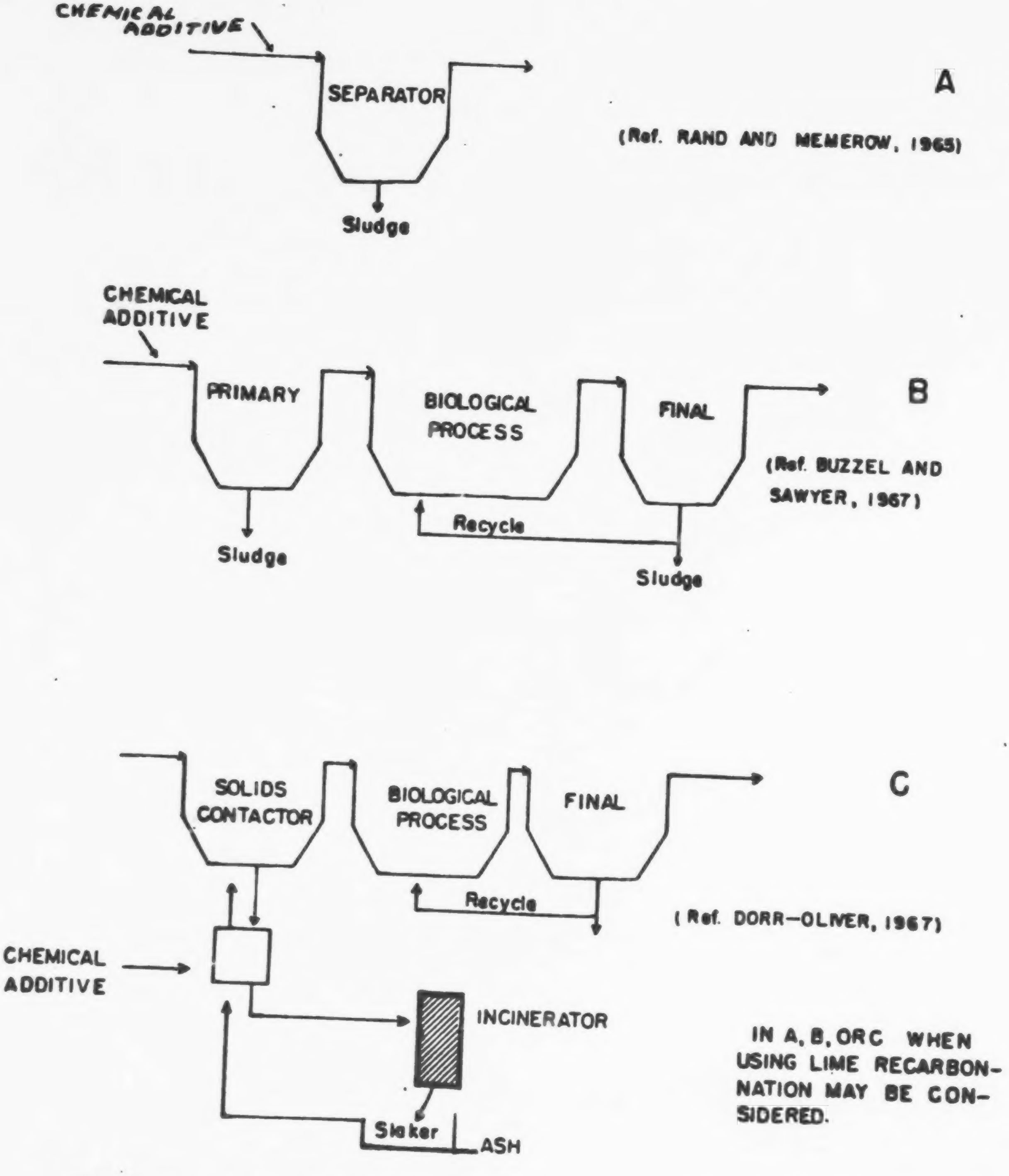
FAIRBORN, OHIO TRICKLING FILTER
(Percent Removals)

Unit efficiency - Primary effluent to final effluent

	Total Phosphorus	COD	S. S.	pH Mode	Al : P
Dosed Filter	63	74	51	7.9	1 : 1
Control Filter	13	75	51	7.8	--

Overall efficiency - Raw waste water to final effluent

	Total Phosphorus	COD	S. S.	pH Mode	Al : P
Dosed Filter	64	83	84	7.9	1 : 1
Control Filter	17	83	85	7.8	--
Entire Plant	37	84	92	7.6	0.3 : 1


CHEMICAL ADDITIVE
SEPARATOR
Sludge
A
CHEMICAL ADDITIVE
PRIMARY
BIOLOGICAL PROCESS
FINAL
B
Recycle
Sludge
Sludge
SOLIDS CONTACTOR
BIOLOGICAL PROCESS
FINAL
C
Recycle
CHEMICAL ADDITIVE
INCINERATOR
Slaker
ASH

(Ref. RAND AND NEMEROW, 1965)

(Ref. BUZZEL AND SAWYER, 1967)

(Ref. DORR-OLIVER, 1967)

IN A, B, OR C WHEN USING LIME RECARBONNATION MAY BE CONSIDERED.

FIGURE 2. CHEMICAL TREATMENT VARIATIONS OF BASIC SYSTEM

TABLE IV. ADVANCED PROCESSES FOR NUTRIENT CONTROL

ION EXCHANGE

ELECTRODIALYSIS

REVERSE OSMOSIS

SORPTION

ELECTROCHEMICAL

DISTILLATION

REUSE AND DISPOSAL OF LIME AND ALUM SLUDGES

by

Robert B. Dean
Chief, Ultimate Disposal Research Program
Advanced Waste Treatment Research Laboratory

Second Technical Session
2:45 P.M.
Wednesday, February 5, 1969

Symposium on Nutrient Removal and Advanced Waste Treatment
Portland, Oregon

I. Removal of phosphates by lime leads to sludge that must be disposed of.

A. Chemical equations representing removal of phosphate by calcium hydroxide and aluminum sulfate

$Ca(OH)_2$ Treatment

$$3\ HPO_4^{=} + 5\ Ca(OH)_2 \longrightarrow Ca_5(OH)(PO_4)_3 \downarrow + 6OH^- + 3\ H_2O \qquad (1)$$

Equations 2 and 3, which are the lime softening reactions, also occur:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ CaCO_3 \downarrow + 2\ H_2O \qquad (2)$$

$$Mg(HCO_3)_2 + 2\ Ca(OH)_2 \longrightarrow 2\ CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2\ H_2O \qquad (3)$$

B. $Ca_5(OH)(PO_4)_3$ (hydroxyapatite) is the most stable form at pH's greater than 7-7.5, but precipitation is slow unless there is a large excess of OH^-. The precipitates indicated by "↓" settle in the sludge together with other insoluble material.

C. Lime recovery

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (4)$$

$$Mg(OH)_2 \longrightarrow MgO + H_2O \qquad (5)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (6)$$

MgO does not dissolve in water at normal temperatures.

D. Treatment of sludges

1. Thicken. Recycle supernatant.
   a. Conventional circular clarifiers are effective either upflow or downflow with scrapers. Lime sludge settles well but is retarded by large quantities of $Mg(OH)_2$.
   b. Lagoon.

2. Recarbonate. Recarbonation with CO_2 to pH 9.5 redissolves $Mg(OH)_2$, makes filtration and centrifugation easier. $Mg(HCO_3)_2$ stream cannot be recycled and could cause problems at some locations.

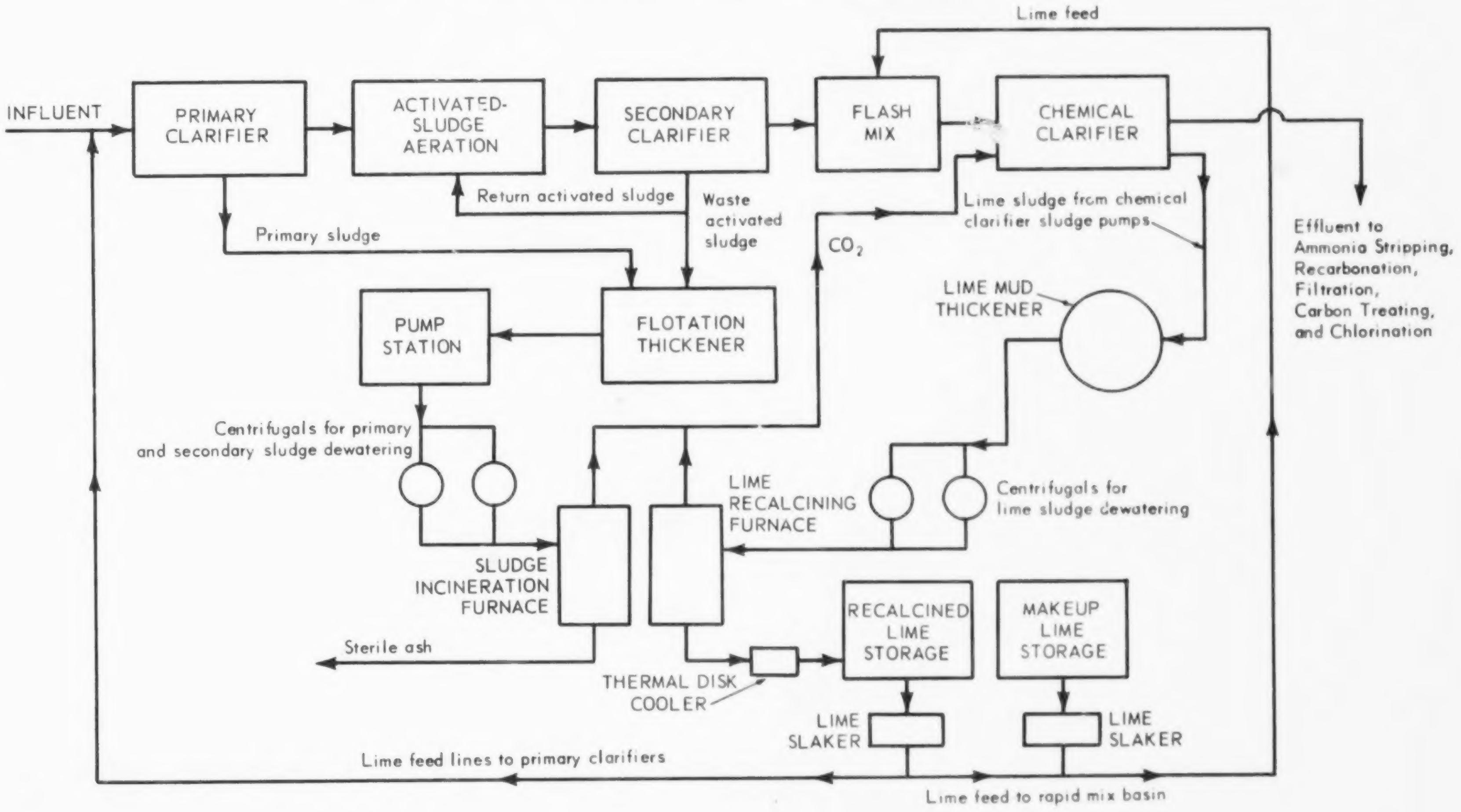
3. Dewater. Recycle supernatant.
   a. Centrifuge--as at Lake Tahoe. Figure 1. Suhr '68.
   b. Filter--rotary vacuum filter or pressure filter.

4. Recalcine. Capture fly ash and odors. CO_2 to atmosphere. See Crow '60, Wertz '60.
   a. Multiple hearth furnace--Lake Tahoe.
   b. Fluidized bed incinerator.
   c. Horizontal rotary kiln--large scale. May have trouble with dirty lime.

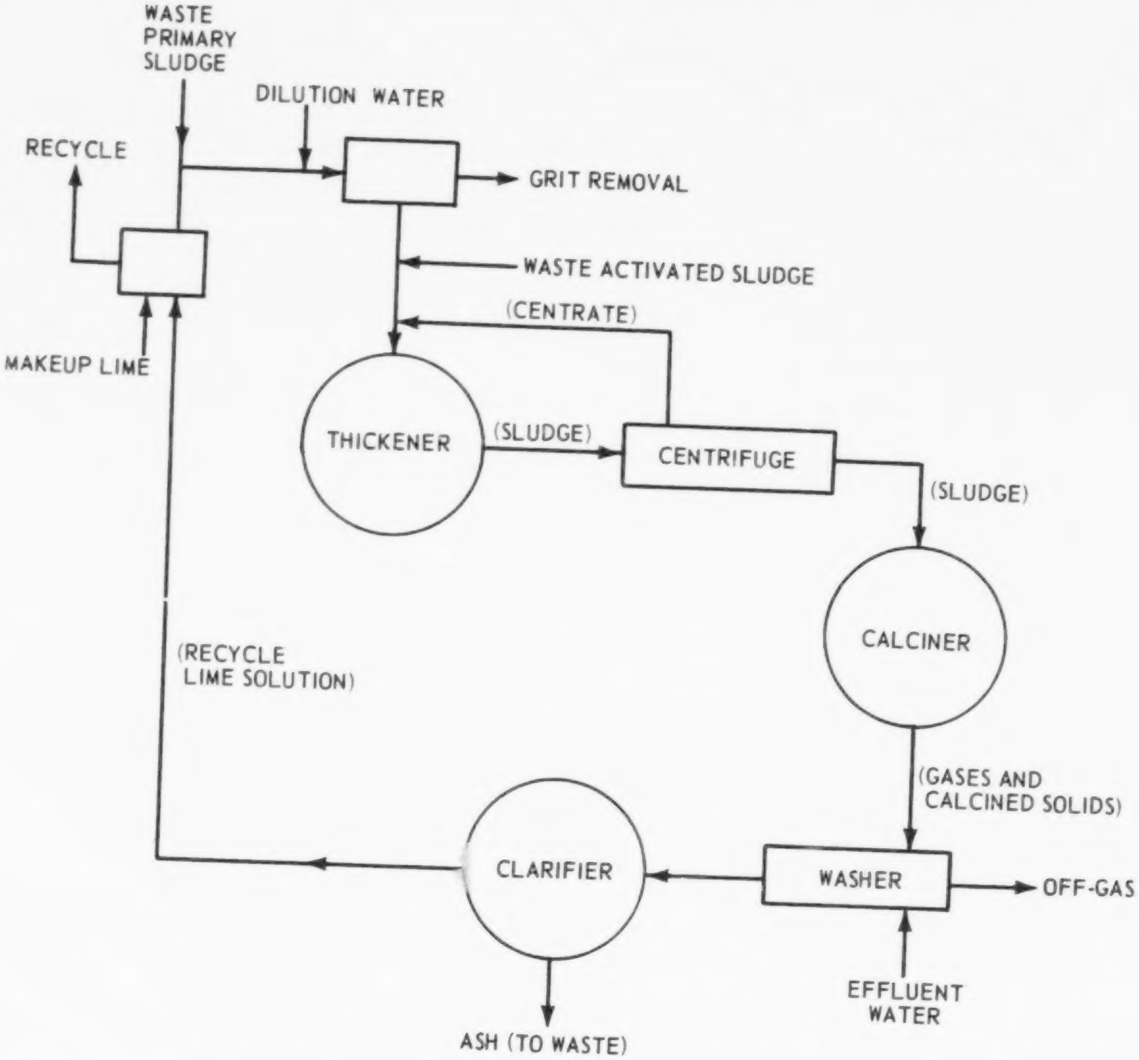
5. Slake. $CaO + H_2O \longrightarrow Ca(OH)_2 + \underline{heat}$. Insolubles (ash) serve as a filter aid and sludge conditioner.
   a. Slurry. Cheapest for clean lime.
   b. Paste--easier to adjust to dirty lime.
   c. Dissolve $Ca(OH)_2$. Solubility 1600 mg/l at room temperature. Discard ash. PEP process. Dorr-Oliver. Figure 2.

6. Discard excess.
   a. Land fill. $Ca_5OH(PO_4)_3$ is not soluble in water.
   b. Lime fertilizer. Excess $Ca_5OH(PO_4)_3$ is available to plant roots.
   c. Soil stabilizer for roads.
   d. See Mulbarger '68.

Phosphate Removal at South Lake Tahoe, with Lime Recalcination and Reuse


Lime feed
INFLUENT
PRIMARY CLARIFIER
ACTIVATED-SLUDGE AERATION
SECONDARY CLARIFIER
FLASH MIX
CHEMICAL CLARIFIER
Return activated sludge
Waste activated sludge
Primary sludge
CO_2
Lime sludge from chemical clarifier sludge pumps
Effluent to Ammonia Stripping, Recarbonation, Filtration, Carbon Treating, and Chlorination
LIME MUD THICKENER
PUMP STATION
FLOTATION THICKENER
Centrifugals for primary and secondary sludge dewatering
LIME RECALCINING FURNACE
Centrifugals for lime sludge dewatering
SLUDGE INCINERATION FURNACE
RECALCINED LIME STORAGE
MAKEUP LIME STORAGE
Sterile ash
THERMAL DISK COOLER
LIME SLAKER
LIME SLAKER
Lime feed lines to primary clarifiers
Lime feed to rapid mix basin

Solids Handling and Lime Recovery in PEP System


WASTE PRIMARY SLUDGE
DILUTION WATER
RECYCLE
GRIT REMOVAL
WASTE ACTIVATED SLUDGE
(CENTRATE)
MAKEUP LIME
THICKENER
(SLUDGE)
CENTRIFUGE
(SLUDGE)
CALCINER
(RECYCLE LIME SOLUTION)
(GASES AND CALCINED SOLIDS)
CLARIFIER
WASHER
OFF-GAS
EFFLUENT WATER
ASH (TO WASTE)

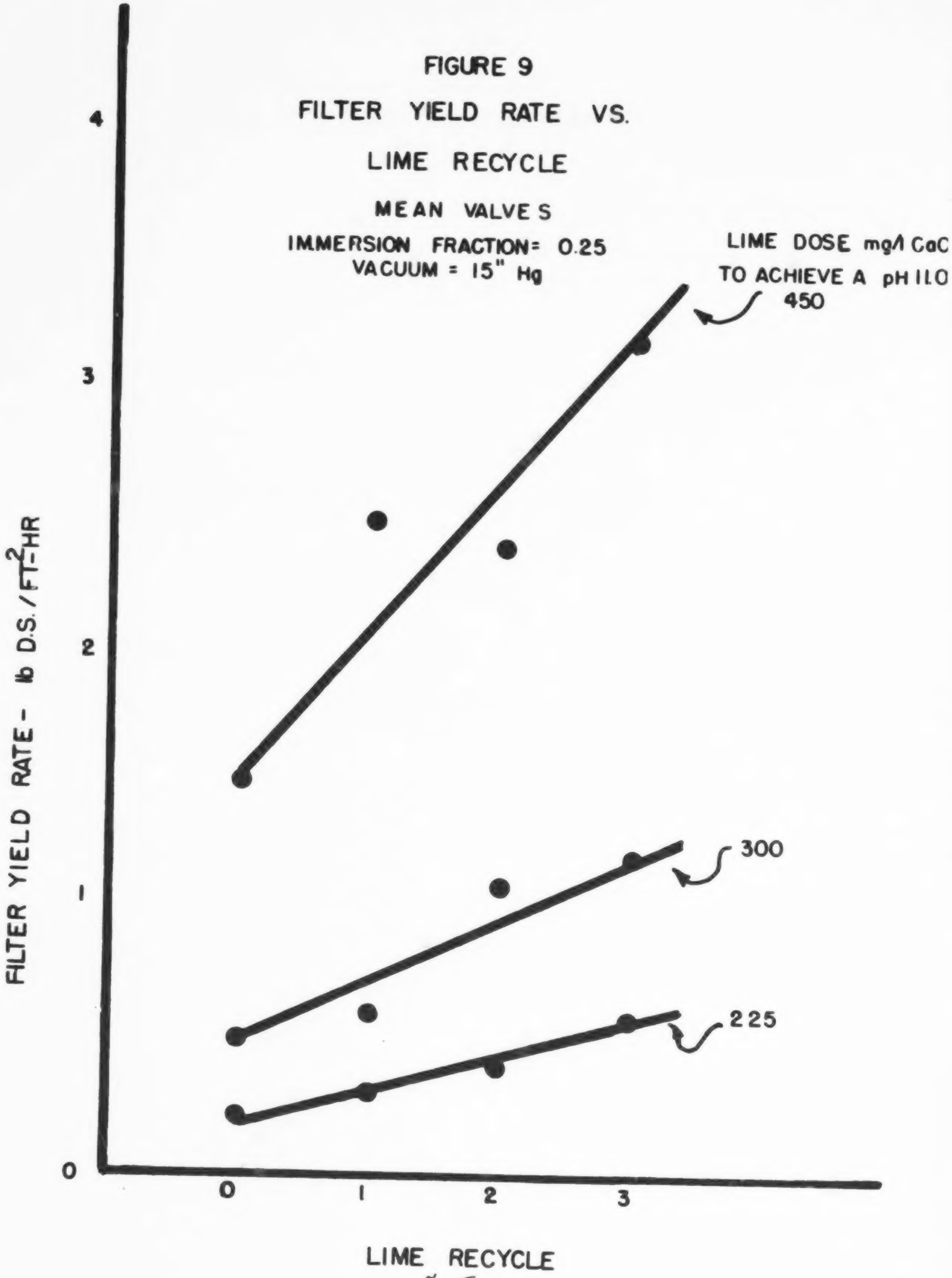


FIGURE 9

FILTER YIELD RATE VS. LIME RECYCLE

MEAN VALVES

IMMERSION FRACTION= 0.25
VACUUM = 15" Hg

II. Removal of phosphates by aluminum hydroxide. See Lea '54, Stumm '68.

A. Chemical equations.

Influence of pH on Al^{+3} form:

$$\begin{array}{ccccc} Al^{+++} & \xrightleftharpoons{+3OH^-} & Al(OH)_3\downarrow & \xrightleftharpoons{+OH^-} & Al(OH)_4^- \\ \text{pH 3} & & \text{pH 7} & & \text{pH 12} \end{array} \qquad (7)$$

Phosphate removal:

$$2Al(OH)_3 + HPO_4^{=} \longrightarrow AlPO_4 \cdot Al(OH)_3\downarrow + 2OH^- + H_2O \qquad (8)$$

1. Phosphate removal is a function of pH and other constituents of waste stream. Optimum near pH 7.

2. Alumino phosphate shown is not a pure compound and may contain calcium. Approximately 2 moles of Al are required per mole of P. Figure 3.

B. Treatment of sludges.

1. Thicken. Neubauer '68.
   a. Lagoon. Ineffective. Never solidifies. Maximum of about 8-10% solids.
   b. Freezing. Very effective if done slowly. Doe '67 and Christensen. Expensive if artificial freezing is required. 125 kwh/1000 gal.
   c. Sand beds.
   d. Precoat vacuum filter.
   e. Pressure filter with lime.
   f. Centrifuge. Ineffective.

2. Filtrate or supernatant can be recycled. If lime is used, this may contain useful aluminate.

3. Solids can be used for land fill if 20% or greater.

REMOVAL OF PHOSPHATE FROM WASTEWATER BY ALUMINUM HYDROXIDE

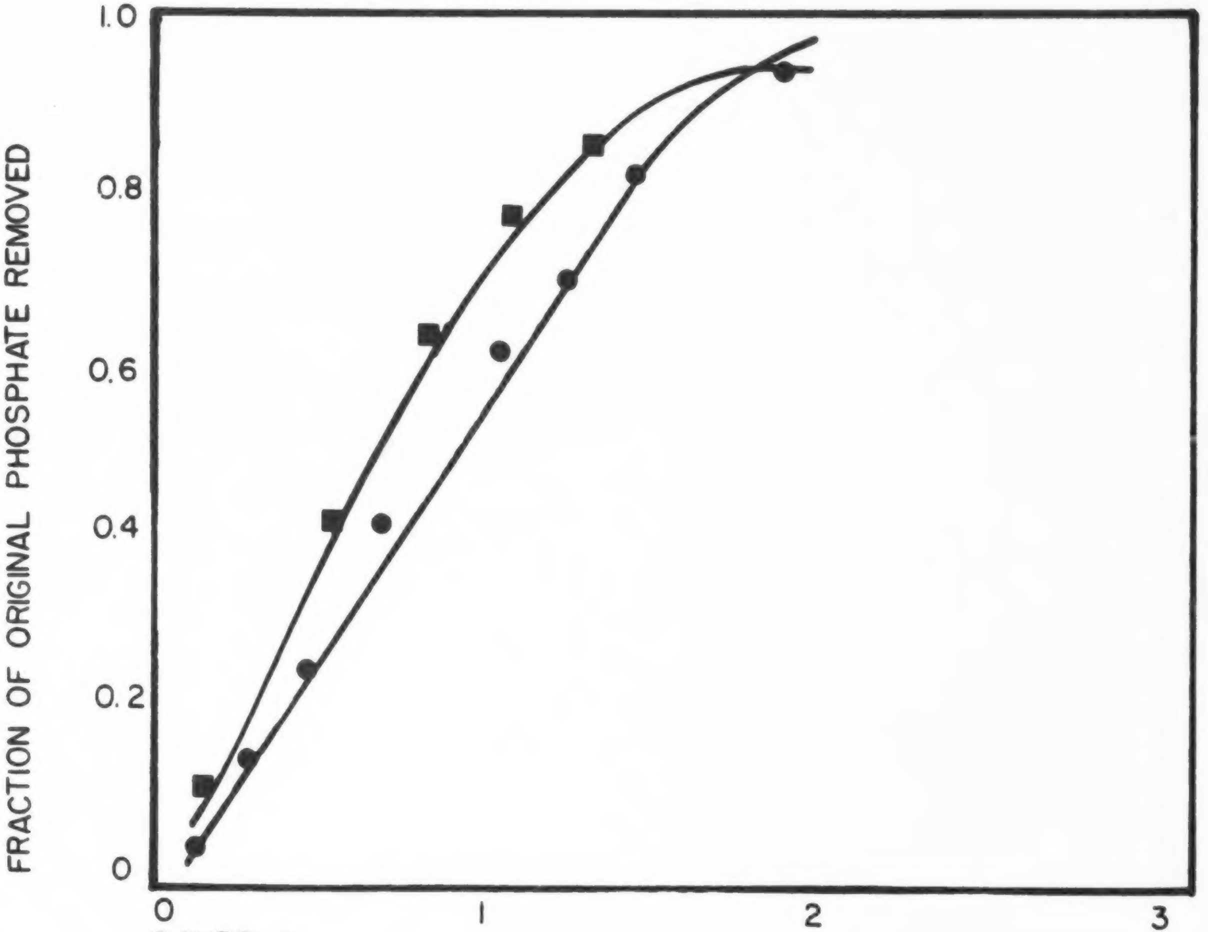


FIGURE 3

4. Recovery with alkali. See Lea '54, Slechta '67.

Solubilization:

$$3AlPO_4 \cdot Al(OH)_3\downarrow + 5Ca(OH)_2 + 6OH^- \longrightarrow 6Al(OH)_4^- + Ca_5OH(PO_4)_3\downarrow \quad (9)$$

Loss of aluminum ions as calcium aluminate precipitate:

$$Ca^{++} + 2Al(OH)_4^- \longrightarrow Ca[Al(OH)_4]_2\downarrow \quad (10)$$

a. Aluminate may be reused in process.
b. May need heat. Requires large vessels. Process works best at high dilutions avoiding precipitation of calcium aluminate.
c. Up to 75% recovery as aluminate balances acidity from makeup alum. Higher recoveries of Al are unlikely.
d. Heat treatment of sludge improves filterability.

5. Acid recovery does not separate alum from phosphate and recycle is not practical.

Pertinent Literature

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Slechta, A. F., and Culp, G. L., "Water Reclamation Studies at the South Tahoe Public Utility District," Journal Water Pollution Control Federation, 39, No. 5, 787 (May 1967).

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Webster, J. A., Daer Alum Recovery Plant, J. Instn. Water Engrs., 20, No. 2, 167-98 (1966)

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ALTERNATIVE METHODS OF PHOSPHORUS REMOVAL

Jesse M. Cohen, Chief
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Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio

Technical Seminar
Nutrient Removal and Advanced
Waste Treatment
Portland,Oregon
February 5 and 6, 1969

ALTERNATIVE METHODS OF PHOSPHORUS REMOVAL

J. M. Cohen

INTRODUCTION

It would be remiss if this conference were to end with the impression that removal of phosphorus can be obtained only by reagents consisting of iron, aluminum or lime. At the present time, these are the reagents of choice; they have been shown to be effective in precipitating phosphate, the technology and the engineering design have been fairly well advanced from small pilot-scale operation to relatively large application. The costs have been shown to be reasonable. The purpose of my talk is to point out that there are alternative methods for removing phosphates. At the present state of development, these processes are clearly not competitive. The research for some of these methods is just getting started. It is entirely possible that some of these alternative processes will never be competitive for the large waste treatment plant that can afford the capitalization; the skilled operation and required manpower to operate a removal plant based, say, on lime precipitation and calcination. Special circumstances - perhaps the relatively small treatment plant may dictate the selection of a process that has a higher unit cost for removing phosphates but which requires less attention.

ACTIVATED ALUMINA

One alternative process that has good prospects is the removal of phosphates by activated alumina. Activated alumina is a synthetic material consisting largely of aluminum oxide which has been activated at high temperature. It is available in a variety of forms ranging from fine powders to granules. A particular property is its high specific surface area ranging from 200 - 400 square meters per gram. In this respect it is similar to activated carbon which has surface areas of $\approx$ 800 - 1000 m^2/gram.

The ability of activated alumina to remove phosphates and some data to support this contention was published only as recently as 1966 by Yee working at the Oak Ridge National Laboratory. Not only could phosphate be sorbed from solution by activated alumina but, most importantly, the sorbed phosphate can be quantitatively desorbed by appropriate regeneration chemicals. In this respect, alumina behaves like an ion-exchange material but with some significant differences, as I will point out later. The probable mode of operation would be column contactors, much like those in current use for activated carbon. These require, as you know, reduced capital costs and a minimum of direct labor costs. The principal cost is that of the alumina itself, and especially the cost of the regenerating chemicals and their final disposal.

There are a great variety of activated aluminas available, varying greatly in unit cost and capacity to sorb phosphates. Yee, tested three commercially available types and this information is shown in Figure 1.

*Evaluation of Three Commercial Aluminas**

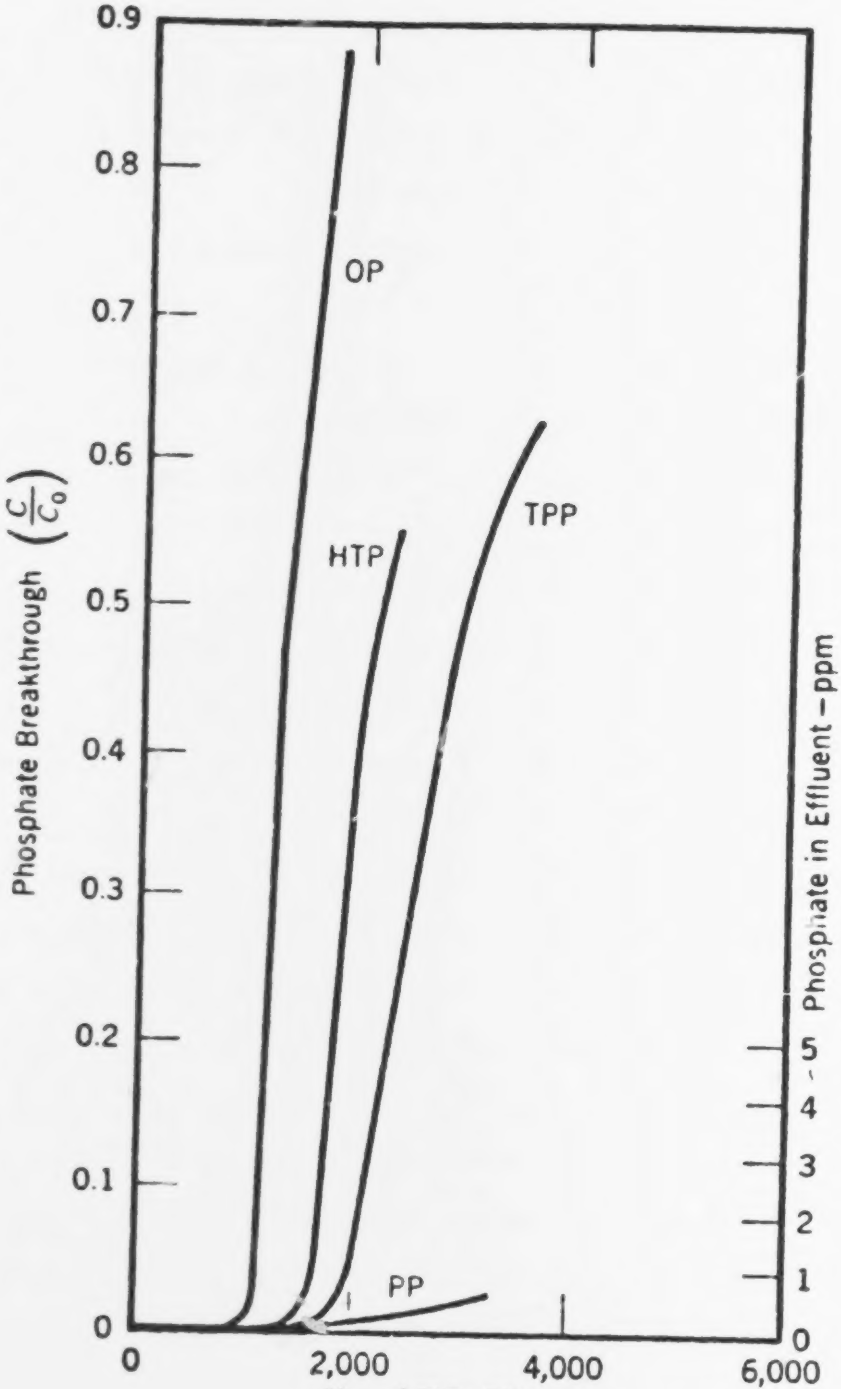
Item	Type of Alumina		
	A	B	C
Cost—*¢/lb*	12	100	40
Surface area—*sq m/g*	250	250	400
Alumina sorption capacity for mixed phosphates (as PO_4^{3-})—*mg/g*	19	17	>27
Mixed phosphates (as PO_4^{3-}) eluted from alumina in regeneration—*mg/g*	17	10	28
Regenerant waste—*BV's*	12	16	12
Alumina dissolved in regeneration—*per cent*	8	5	35

* Performances were evaluated in upflow through fluidized beds.

The aluminas were packed in columns and were then fed solutions containing phosphorus in a variety of forms such as orthophosphate, tripolyphosphate, pyrophosphate and hexametaphosphate. Flow rates were of the order of 0.25 to 1.25 gallons per minute/sq ft, about the rates normally used for an ion-exchange process.

It is clear from this table that of the three aluminas that were tested only one, type A, would have commercial value for phosphate removal, based on its lowest cost, 12¢/lb and more importantly on the low solubility during regeneration. Also note that regeneration is almost complete - 17 mg/gram of phosphate was recovered from a loading of 19 mg/gram. These data, incidentally, were obtained from a pilot-plant operation rather than the bench-scale work previously referred to.

Some breakthrough curves are shown in the next slide, Figure 2. The curves represent removal patterns for various forms of phosphate by plotting bed volumes versus a ratio of influent to effluent phosphate concentration. The smaller the value the greater the removal. With a feed concentration of 25 ppm of phosphate, which is about what most wastewaters will contain, phosphate ion could not be detected until more than 1000 bed-volumes had passed - providing more than 99 percent removal. No process that I know of obtains such complete phosphate removal. Also note that alumina removes polyphosphates even better than orthophosphate, with breakthrough curves indicating ≈ 1800 bed volumes before breakthrough. As a "polishing" process to remove the last trace of phosphate after conventional treatment had reduced the concentration to say 1 ppm, alumina may be very appropriate. Under these conditions better than



Phosphate Sorption on Type A Activated Alumina

99 percent removal would be obtained while processing 20,000 bed volumes of treated effluent and producing only about 10 bed volumes of regenerant, a volume reduction factor of about 2000.

Time will permit only a brief listing of the additional advantages of alumina.

1. Alumina is highly selective for phosphate and removes polyphosphates even better than the orthophosphates.

2. In contrast to alum, iron or calcium salts, no additional inorganic ions are added.

3. Treatment with alumina does not affect pH.

4. Variations in feedwater composition and quality have little or no effect on removal efficiency.

5. Removal efficiencies are so high that extremely low residuals are achieved, of the order of 0.05 ppm of phosphate.

Based on Yee's work, chemical costs can be estimated at 3.9 cent/1000 gallons for a feed containing 14 mg/l of phosphate ion and 6.4 cents/1000 gallons for a feed of 23 mg/l. These estimates assume an 8 percent loss of alumina for each regeneration cycle, when in fact, cycles after the second amounted to only 5 percent.

Activated aluminas have a wide spectrum of structural and sorptive characteristics. Additional research should reveal the effect of these properties on phosphate removal capacity. There is some evidence that capacity can, in fact, be increased. The current regeneration system using sodium hydroxide followed by reacidification with nitric acid may not be best, and alternate systems based perhaps on ammonium hydroxide which would enable regenerant recovery and reuse should be investigated. Efforts are currently being made in this direction.

Precipitation by Lanthanum

In the search for reagents which produce insoluble salts with phosphate compounds, it was natural to consider very early the common precipitants based on aluminum, iron and calcium. Another metal which we are considering is lanthanum. Although the use of this salt may appear to make the process prohibitively expensive, the possible greater efficiency of the phosphate removal coupled with the use of a regeneration step could make this approach attractive. The solubilities of the metal phosphates are shown in the next slide (Slide). The solubilities in terms of mg/l of phosphorus were calculated from reported solubility products. It is clear that lanthanum phosphate is about as insoluble as iron and aluminum phosphate. In practice, however, these theoretical solubilities are not obtained with iron or aluminum even though large excesses of precipitants are added. The reasons apparently are that competing hydrolysis reactions reduce the concentration of metal ions available for phosphate precipitation. This basis has been used to explain the lower solubility of aluminum phosphate despite the fact that its solubility product is greater than that of ferric phosphate. Non-hydrolyzing calcium added to wastewater in dosages several times greater than those of aluminum or iron reduces residual phosphate to about the same level although the theoretical solubility of calcium hydroxyapatite, the form of the precipitate, is 6-7 orders of magnitude greater than the iron and aluminum phosphates. In short, solubility product is not an accurate guide to the practical usefulness of a precipitant. It should be remembered that solubility product represents equilibrium conditions and does not consider kinetics. Thus, rate of precipitation is also an important consideration.

SOLUBILITY OF PHOSPHATES

SALT	K_{SP}	CALCULATED SOLUBLE P MG/L
$FE\ PO_4$	10^{-23}	9×10^{-8}
$LA\ PO_4$	3.75×10^{-23}	2×10^{-7}
$AL\ PO_4$	10^{-21}	9×10^{-7}
$(MG)_3(PO_4)_2$	2×10^{-27}	0.1
$CA_{10}(OH)_2(PO_4)_6$	10^{-90}	0.3

The extent of removal of phosphate by hydrolyzing metal ions like iron and aluminum really is a function of both solubility product, rate of reaction and importantly, of the competing hydrolysis reactions. Laboratory studies have shown that both aluminum and iron form soluble complexes in the presence of large excesses of either the metal or phosphate ions. Moreover, under certain conditions a stable colloidal precipitate which was difficult to remove from suspension was formed. These studies showed that lanthanum is, 1) only slightly hydrolyzed, and 2) shows less tendency to form soluble complexes with phosphate. These factors led us to consider the technical feasibility of using lanthanum as a phosphate precipitant.

To be successful, certain fundamental criteria would have to be met: 1) the phosphate should be readily reduced below 0.1 mg/l of phosphorus; 2) the residual La^{+3} in solution should be negligible and 3) recovery and reuse should be inexpensive.

A quick test in our laboratories produced the data shown in the next slide. (Slide). The sample of wastewater used in this test was collected after a day of rain and hence showed a low phosphorus content. A dosage of 23 mg/l of lanthanum added as lanthanum nitrate reduced the phosphorus residual to just detectable concentration - 0.1 mg/l of P. Also note that turbidity was reduced to 4 units.

When we first considered lanthanum as a precipitant, our enthusiasm was curbed because the then current price was $3.00 a pound of lanthanum oxide. A more recent price quotation of 60 cents a pound for a lanthanum-rich mixture of rare earths is certainly more encouraging. Clearly,

PRECIPITATION OF PHOSPHATE WITH LANTHANUM

MG/L LA	SAND-FILTERED TURBIDITY	SAND-FILTERED ORTHO-P
0	17	1.2
23	4	0.1
46	0.6	< 0.1
69	0.4	< 0.1
92	0.9	< 0.1
139	1.5	< 0.1

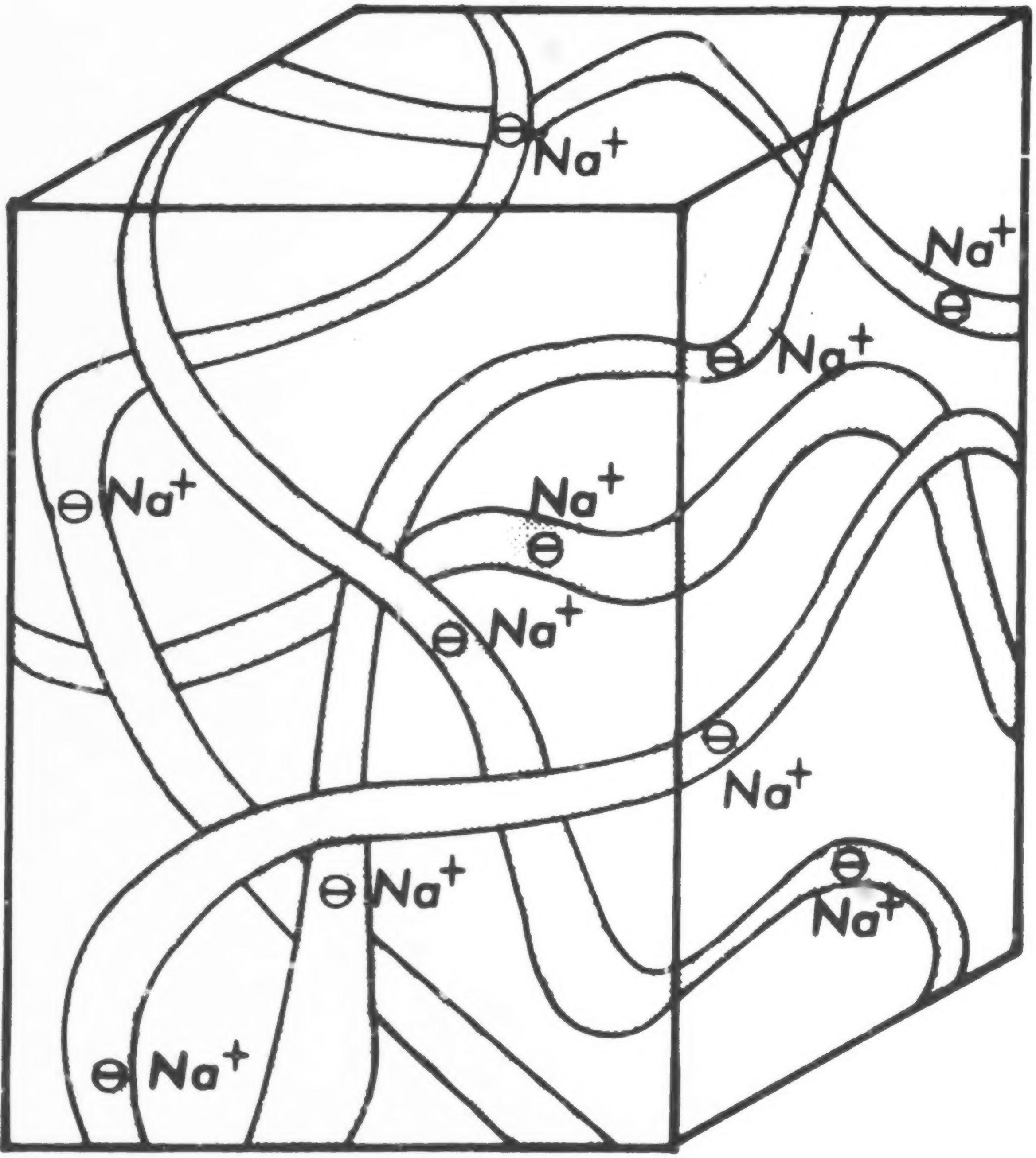
it is not yet competitive with 3 cents a pound alum. To become competitive it will be necessary to use virtually stoichiometric dosages of lanthanum to maintain low residuals of lanthanum in the effluent. But since the phosphate concentration in the wastewater is constantly changing, some means will have to be worked out to adjust lanthanum additions to phosphate changes.

And, finally, methods will have to be developed to recover the lanthanum with high efficiency. From desk-top considerations an alkali regeneration process appears to be promising. Use of lanthanum for phosphate removal will be explored for technical feasibility.

Ion Exchange

Ion exchange materials, both natural and synthetic, have potential for removing phosphates from wastewater, although the primary function is the removal of inorganic ions in general. But modifications can be made on natural ion-exchange materials to obtain a degree of selectivity for phosphate ion, in which case, ion-exchange as a process for phosphate removal becomes more attractive.

A typical ion-exchange material can be looked upon as a microporous matrix containing many ionic sites, either all positive or all negative as shown in the next slide (Slide). In order to maintain electro-neutrality, each fixed ionic site must have associated with it and ion of opposite charge or counter ion. This counter ion must be mobile enough so that it can be replaced by, or exchanged for, another ion of the same charge upon contact with a solution of this new ion.


⊖ Na+
Na+
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TYPICAL EXCHANGE MATERAL

When all of the original counter ion is replaced, the ion-exchange material is exhausted. A concentrated solution, 4 to 10 percent, of the original counter ion must be used to regenerate the ion exchanger. Depending on the counter-ion the exchange material can be either a cation or anion exchanger.

The most important group of natural ion-exchange materials are the zeolites and clay minerals. These materials are largely alumina silicates which generally carry a net negative charge and hence are dominantly cation exchange materials. But certain of the clay minerals are capable of exchanging anions as well. For example, exchange of hydroxyl ion for chloride, sulfate or phosphate ions has been observed in montmorillonite, kaolinite and certain feldspars and micas. The problem with these naturally occurring ion-exchangers is that anion capacity is low - generally less than 10 percent of the cation exchange capacity.

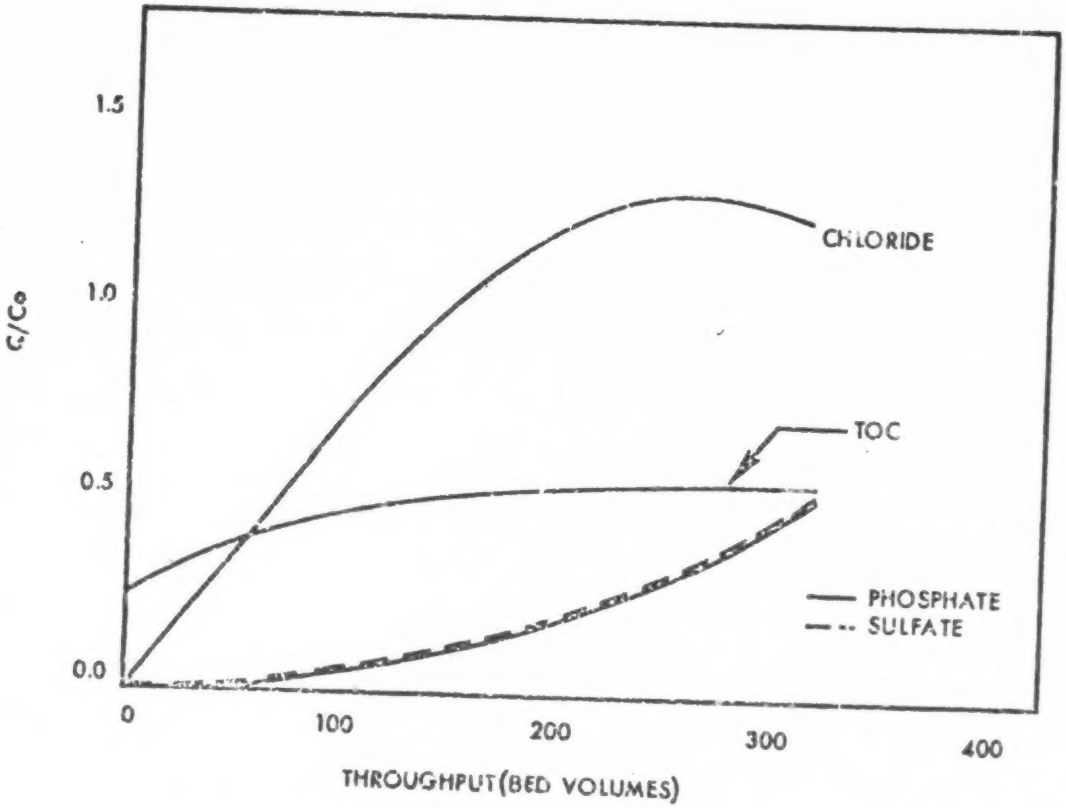
It is technically possible, however, to chemically treat the natural mineral so that replacement of certain ions in the clay structure occurs with iron or aluminum ions. These replacement ions can now react with phosphate ions. Depending on the degree of replacement obtainable by chemical modification one can expect increasing capacity to react with phosphate. It should be possible to regenerate the clay mineral by stripping the phosphate off with some regenerating reagent.

Currently, this concept is in its barest infancy. We know that these minerals have some natural phosphate exchange capacity but it is too small to be useful. It's been shown that this capacity can be increased by appropriate chemical modification. How much increase remains to be determined. The process could become attractive economically since the raw materials, clay minerals, are abundantly available and cheap - just cents a pound. If chemical modification costs are modest and if the increase in exchange capacity is reasonable then the process could find use for phosphate removal. At the present time a modest research program is being directed toward developing this treatment concept.

The most important ion-exchange materials are the synthetic organic types with which all of you are undoubtedly familiar. Synthetic anion exchangers have adequate capacities to remove anions from the water. The problem is that there is competition among the various anions for the exchange sites; thus the selectivity of the resin for phosphate ion becomes a critical factor. The competition is not random but is dictated by considerations of ionic size and ion valence. This selectivity can be illustrated by the breakthrough patterns shown in the next slide.(Slide).

In alkaline wastewater, the dominant phosphate species is the HPO_4 double negative. The resin selectively exchanges this ion in preference to Cl^-, NO_2^-, or NO_3^-. Unfortunately, the resin has about the same preference for sulfate ion as for phosphate, thus the anion exchange capacity must be shared with the two anions. The problem here is that wastewater generally contains 2 to 5 times as much sulfate as phosphate ion, thus effectively reducing the capacity to remove phosphate ion.

In order for synthetic ion-exchange materials to become a competitive process, they must become highly selective for phosphate ion. Such selective resins have been developed for certain ions such as potassium, fluoride and borate. None, to my knowledge, has been developed for phosphate ion, and until such materials are made, synthetic ion exchange will not be economically useful for removing phosphate.



BREAKTHROUGH PATTERNS FOR ANION EXCHANGE

REMOVAL IN SOIL SYSTEMS

One of the processes for removal of phosphates that has generally been overlooked is use of naturally occurring soil. Soil systems as treatment devices, rather than as means of disposal, are receiving more attention as a potentially cheap method of treating wastes.

Soil is a composite medium that may contain relatively inert rock, gravel and sand as well as reactive clays and minerals; and additionally, varying amounts of organic materials such as humus, living and dead vegetable and animal matter. Many of the components possess useful properties to accomplish effective waste treatment. Treatment mechanisms include biological oxidation, chemical precipitation, ion-exchange, adsorption, chemical oxidation and plant assimilation. The sum total of these effects is capable of providing very effective treatment of wastewater.

A major effect is the removal of phosphates by the soil system. The potential capacity of soil to remove phosphate is enormous. Actually, hydraulic failure is more likely to occur well before the phosphate removal capacity has been taxed. Data we have obtained from field and lysimeter studies at Westby, Wisconsin, and Loveland, Ohio, are shown in the next slide. (Slide). These data were collected over a number of years. In almost every instance, better than 90 percent of the phosphorus was removed by a six-foot depth of soil. Phosphate removal was not greatly affected by seasonal variation, vegetation, or anaerobic soil conditions. Other data we have obtained show that most of the phosphate, approximately 75 percent, is actually removed by the upper 1-foot layer of soil.

EXPERIMENTAL RESULTS

PHOSPHATE REMOVAL IN SILT LOAM

	INFLUENT P MG/L	6 FT PERCOLATE MG/L	PERCENT REMOVAL
WESTBY			
SOIL & VEGETATION	9.7	2.4	75[(1)]
SOIL & VEGETATION	9.7	0.7	93
LOVELAND			
BARE SOIL, WINTER	6.3	0.3	95
BARE SOIL, SUMMER	11.5	0.2	98
SOIL & VEGETATION, SUMMER	11.5	0.15	99
BARE SOIL, ANAEROBIC	13	1.0	92

(1) 1 FT PERCOLATE

More important to this discussion is the fact that these systems had by no means begun to exhaust the potential for phosphate removal. The next slide (Slide) shows the phosphate loadings in our studies as compared to reported capacities. In the 6 years of field operation at Westby, Wisconsin, 1.6 tons of phosphorus had been fixed in the upper 6 inches of an acre of soil. Capacities for some coastal sandy soils range from 11.2 to 40 tons of phosphorus per acre half-foot. Some coastal sandy soils have capacities ranging upward to 205 tons per acre half-foot. It is obvious that only a very small portion of the potential capacity had been used at either Westby or Loveland. Both of these operations were operated at about 1 gallon per day/sq ft. At this rate the phosphorus capacity would not be exhausted for upwards of a century.

The mechanisms for phosphate fixation in the soil are complex and can be attributed to many factors. Among the more important are: type of soil, particle size, pH, reduction potential, temperature, organic content and reaction time. All of these factors contribute to the mechanisms of anion exchange and adsorption, chemical precipitation and assimilation into organic matter.

The potential of soil to treat wastes and to remove phosphates should not be ignored. When land is available, this method should be considered.

EXPERIMENTAL RESULTS

PHOSPHATE REMOVAL

		DURATION	PHOSPHATE-P REMOVAL (1)
WESTBY SYSTEM (SILT LOAM)		6 YEARS	1.6
LOVELAND SYSTEM (SILT LOAM)		1.5 YEARS	0.4
			CAPACITIES (2)
SASSAFRAS SOIL	p^H 6.5		11.2
COLLINGTON SOIL	p^H 6.5		40
DUTCHESS SOIL	p^H 6.5		35

(1) TONS PER ACRE-HALF-FOOT
(2) BAILEY, FROM TOTH & BEAR, 1947 - THESE ARE SANDY SOILS.

REVERSE OSMOSIS

Phosphates can be removed by the process of reverse osmosis, although the process is being developed principally as a device to remove contaminants in general.

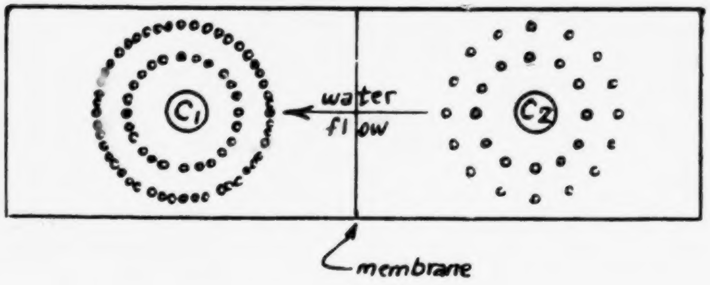
A simple description of reverse osmosis is shown in the next slide. (Slide). When two solutions of unequal salt concentration are separated by a semi-permeable membrane, there is a tendency for pure water to flow from the more dilute to the more concentrated solution. The driving force is the salt concentration gradient. The semi-permeable membrane is simply an imperfect barrier between the two liquids which selectively permits passage of some component of the solution, either solvent or solute.

In the case of osmosis - diagram on the left - (Slide) water passes through the membrane and the inorganic ions are rejected. Under the impetus of the concentration gradient, the water flows through the membrane, and a higher pressure is created in the receiving vessel (called the osmotic pressure); the salt concentrations in the two vessels thus tend to become equal. Now, if additional pressure is applied to the solution already under greater pressure, the water flow will be reversed; that is, water will now flow in the reverse direction, hence the name reverse osmosis or ultrafiltration.

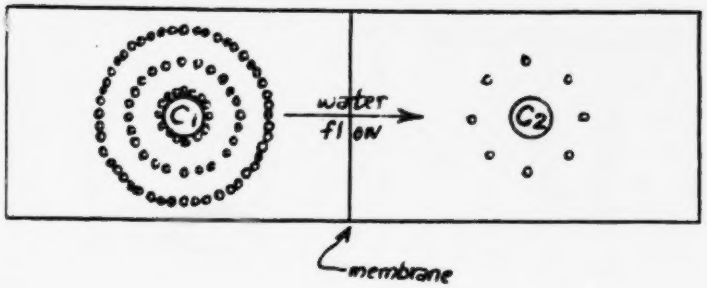
Reference to filtration is appropriate, since water flows from the more concentrated to the more dilute side while salt ions are rejected or filtered. The magnitude of the flow and the degree of salt rejection are dependent upon the applied pressure, the characteristics of the membrane, among other factors.

OSMOSIS AND REVERSE OSMOSIS

Osmosis


C1
water
flow
C2
membrane

Reverse Osmosis, Ultrafiltration, Hyperfiltration


C1
water
flow
C2
membrane

$\boxed{C_1 > C_2}$

Process	Driving Force of Process	Primary Flow	Principal Result
OSMOSIS	concentration gradient	solvent (water)	the concentrations are equalized
REVERSE OSMOSIS	pressure	solvent (water)	pollutants are removed from the water

Membranes can be made with selectivity for certain ionic or nonionic materials, but current research is directed toward development of membranes which remove all contaminating substances. However, as a general rule, ion removal is directly proportional to ion valence, thus multivalent phosphate and sulfate are more readily removed than monovalent chloride.

Large scale tests of reverse osmosis have shown that virtually 100 percent of the phosphate ion is removed by "tight" membranes while 94 percent was removed in the "looser" membranes. A reverse osmosis unit currently available from a manufacturer has been designed to remove organic and particulate matter and to operate at the relatively low pressure of less than 100 pounds per square inch. Ninety-five percent removal of the phosphate ion is claimed. The manufacturer puts the cost of the total treatment, which includes phosphate removal, at about 30 cents per 1000 gallons.

Thus, if reverse osmosis can be developed to an economically useful process for partial demineralization, it is useful to know that phosphate will be almost completely removed.

Sludge Blanket Process

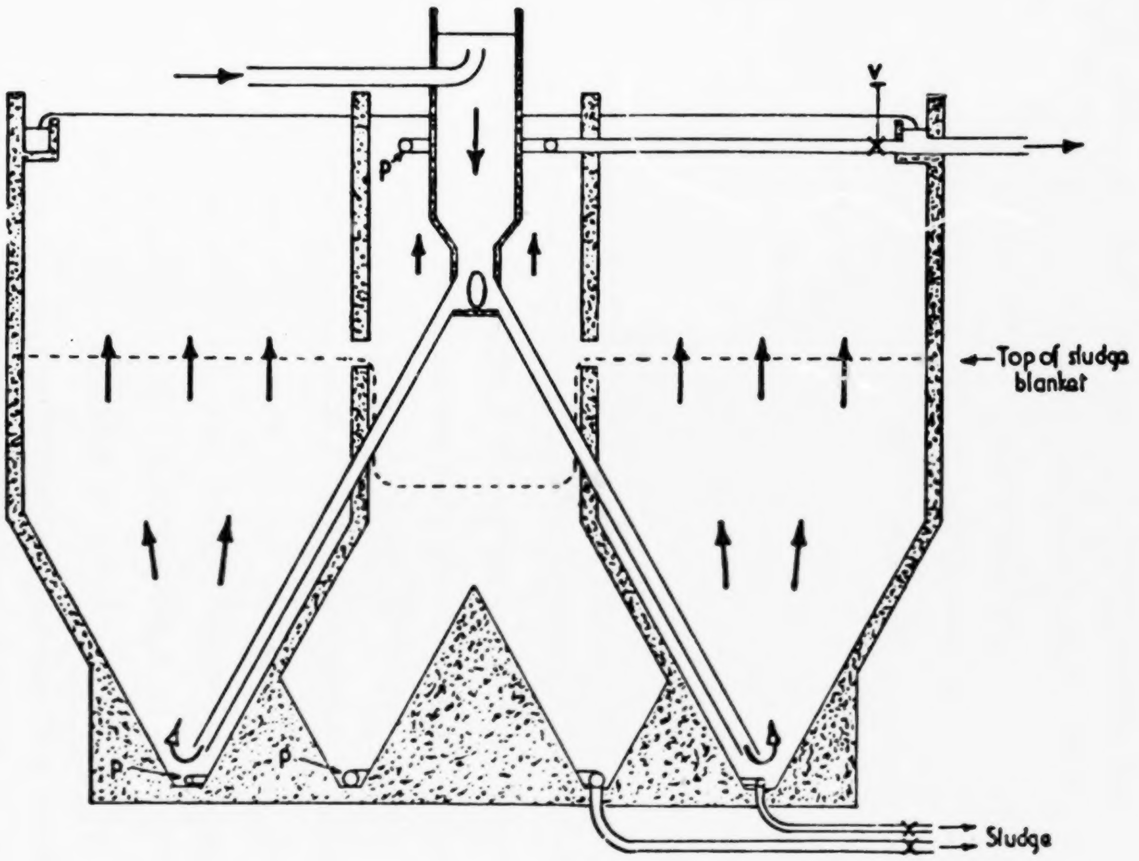
In the final portion of this discussion I would like to comment on the merits of the sludge-blanket or up-flow clarifier. This, of course, is not an alternative method of removing phosphate but rather is an alternative to the widely used horizontal-flow flocculators and sedimentation basins. There are some significant advantages to up-flow clarification. Capital costs for equivalent flows are lower; since the up-flow system requires a single vertically oriented tank with a much reduced detention time, construction costs and land requirements are reduced. Several unit processes take place in a single tank - coagulation, flocculation, sedimentation and sludge removal.

Because of the extremely complicated hydraulics and the multi-functional character of the device, there has evolved a great number of individual designs. For those of you who are not familiar with this type of equipment, the next slide (Slide) illustrates the usual components of a sludge-blanket clarifier.

Incoming wastewater dosed with coagulant enters the unit at the central well and then flows downward to the bottom of the twin tanks which contain a "blanket" of coagulant sludge. The flocculated wastewater is thus caused to flow through the blanket. Clarified supernatant is withdrawn at the top and settled sludge is withdrawn at the bottom.

Upflow clarifiers are operated at rates of 10-15 gal/hr/sq ft which provides detention times of about 1 hour. Sludge volume generally amounts to less than 5 percent of the throughput. The ability of the sludge-blanket device to remove pollutants such as phosphates, suspended solids, color and organic solids is equal to or greater than a corresponding horizontal unit. A major advantage is the intimate contact obtained in the sludge blanket thereby enhancing chemical and physical reactions.

LIBRARY
PACIFIC NORTHWEST WATER LABORATORY



V
P
Top of sludge blanket
P
P
Sludge

CROSS SECTION OF A CIRCULAR UPFLOW REACTOR

(AFTER AITKEN)

Preliminary results in our laboratory with an experimental unit showed phosphate removals of 80-97 percent with blanket depths of 4-8 feet, using alum, ferric sulfate and lime.

We have currently under way a study of this device for application to wastewater treatment.

Concluding Remarks

I hope that these brief remarks on alternative methods for removal of phosphates have made the point that our program of research on phosphate removal is considering methods other than the ones based on alum or lime. I want to emphasize that none of the methods I've discussed is now ready for application. Hopefully, research will make some of them useful for application in specialized instances.

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COMBINED TREATMENT FOR REMOVAL
OF NITROGEN AND PHOSPHORUS

E. F. Barth

ADVANCED WASTE TREATMENT SEMINAR

Portland, Oregon

February 5 and 6, 1969

COMBINED TREATMENT FOR REMOVAL OF NITROGEN AND PHOSPHORUS

Portland, Oregon
February 5 and 6, 1969

The importance of nitrogen removal is much more broadly based than its ability to serve as an algal nutrient in receiving waters. The biological oxygen demand of most effluents is largely due to ammonia.

Plant efficiencies of COD or suspended solids removal have no correlation with nitrogen removal.

By accident of design some plants are efficient for nitrogen removal.

Effective control requires a design that considers the cycle of nitrogen. A three-stage denitrification process has been developed.

The mineral addition process for phosphorus control can be united with the biological denitrification process. Details of this process will be presented, along with tentative cost estimates.

Dentrification can also be accomplished on carbon or sand columns. A brief outline of the denitrification columns at Pomona will be given.

Because most nitrogen compounds are soluble there are only a limited number of strict chemical approaches to nitrogen control.

The following slides will be used and, where available, a reproduction of the slide is attached:

Slide No.	Title
1	Importance of Nitrogen
2	Carbon Oxidation Versus Ammonia Oxidation
3	Plant Efficiencies
4	Flow Diagram - Archbold
5	Nitrogen Cycle
6	Three-Stage Denitrification
7	Objectives of Combined Process
8	Flow Sheet of Combined Process
9	Changes in Composition
10	Mass Balance - Phosphorus
11	Mass Balance - Nitrogen
12	Mixed Liquor Characteristics
13	Effect of Aluminum on Sludges
14	Cost Data
15	View of Pomona Columns
16	Nitrate Concentration Versus Column Time
17	General Data - Pomona
18	Chemical Approaches to Nitrogen Removal

IMPORTANCE OF NITROGEN

NH_3 in effluents can cause DO sag in receiving water

NH_3 is corrosive to copper fittings

1 NH_3 requires 7 plus Cl_2 for breakpoint

NO_2 causes high Cl_2 demand

NH_3 influences Cl_2 contact time

Nitrogen compounds are nutrients

NO_3 can be health hazard

RELATIONSHIP OF CARBON OXIDATION AND NITROGEN OXIDATION

	mg/1	
	Wastewater	Final Effluent
Organic Matter	250	25
Oxygen Demand	375	37
NH_3	25	20
Oxygen Demand	112	90
Total oxygen Demand	487	127
Oxygen Demand Due to NH_3	22%	71%

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Vol. 38(7), 1208-19 (1966)

TABLE III.—Efficiency of COD Removal, Five-Day Averages

Location and Balance Period	Influent (mg/l)	Primary Effluent		Final Effluent		Overall Removal* (%)
		(mg/l)	Removal (%)	(mg/l)	Removal (%)	
Archbold, Ohio						
I	914	538	43	61	89	94
Hamilton, Ohio						
I	598	270	55	62	77	90
II	494	265	36	58	80	87
Lebanon, Ohio						
I	126	100	21	49	51	61
II	332	127	62	69	45	79
Loveland, Ohio						
I	326	326	0	128	61	61
Milford, Ohio						
I	513	381	26	151	60	69
II	651	314	52	161	48	74

* Before mixing with any bypassed waste.

TABLE II.—Efficiency of Suspended Solids Removal, Five-Day Averages

Location and Balance Period	Influent (mg/l)	Primary Effluent		Final Effluent		Overall Removal* (%)
		(mg/l)	Removal (%)	(mg/l)	Removal (%)	
Archbold, Ohio						
I	328	138	58	18	87	94
Hamilton, Ohio						
I	425	183	57	26	86	94
II	303	167	45	10	94	97
Lebanon, Ohio						
I	57	45	21	19	58	67
II	212	73	65	33	55	84
Loveland, Ohio						
I	137	116	15	51	56	62
Milford, Ohio						
I	256	116	55	45	61	82
II	234	98	58	50	49	79

* Before mixing with any bypassed waste.

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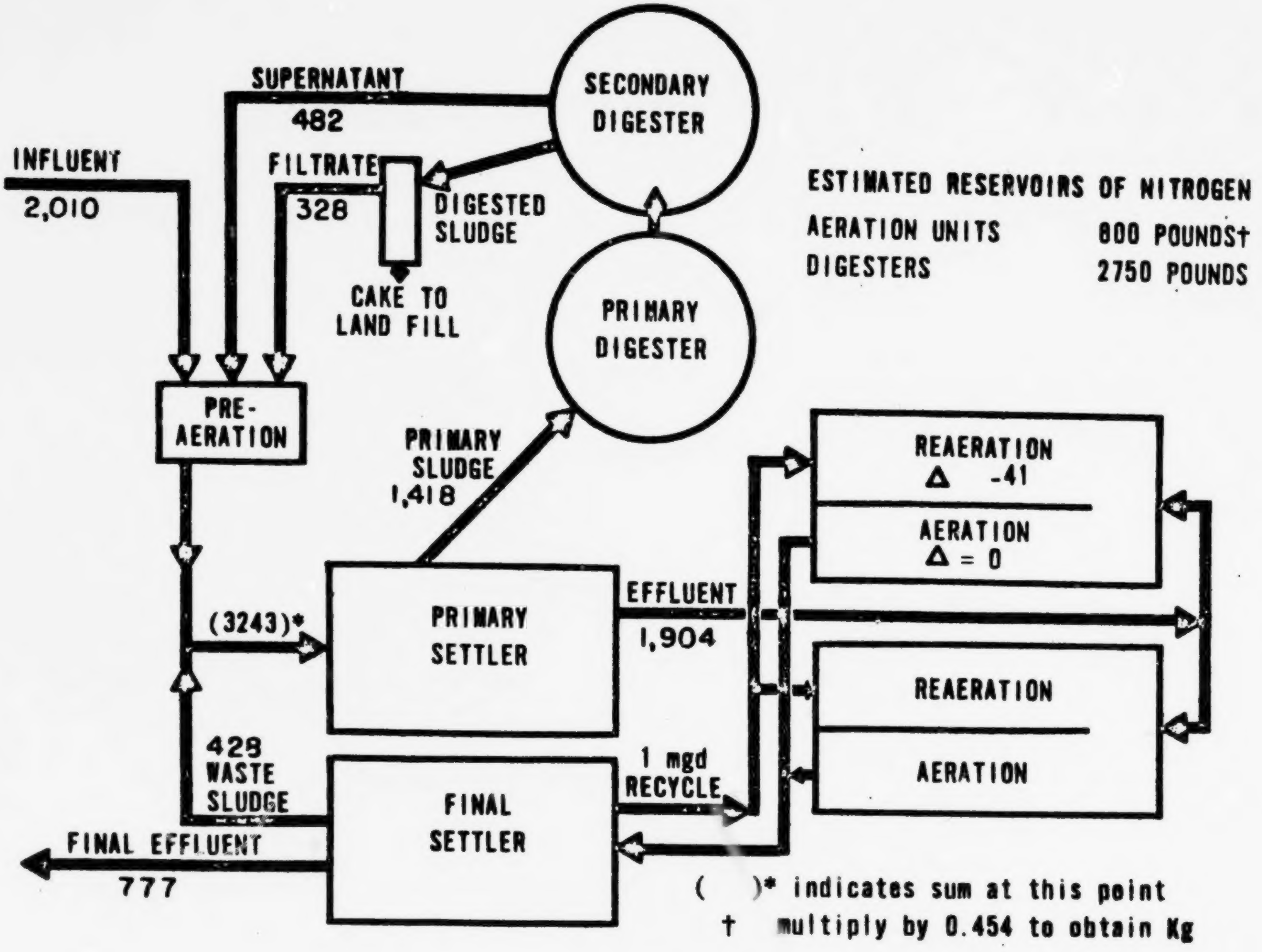
TABLE V.—Nitrogen Removal Efficiencies

Plant and Balance Period	Nitrogen Accounted For (%)		Efficiency of Nitrogen Removal (%)			Nitrification Data (based on nitrogen entering secondary treatment) (%)			
	Primary Treatment	Secondary Treatment	Primary Treatment	Secondary Treatment	Overall Removal	Nitrogen Removed by Denitrification	Apparent Nitrogen Oxidized	Total Nitrogen Oxidized	Nitrogen in Final Effluent Oxidized
Archbold									
I	102	62	9	57	61	38	22	60	56
Hamilton									
I	118	95	−27	31	16	5	0	5	0
II	93	98	2	20	22	2	2	4	3
Lebanon									
I	102	81	5	8	13	19	48	67	69
II	105	76	28	42	58	24	26	50	51
Loveland									
I	101	74	0	30	30	26	10	36	14
Milford									
I	108	86	17	25	38	14	1	15	5
II	97	100	19	8	25	0	1	1	3


SUPERNATANT
482
SECONDARY DIGESTER
INFLUENT
2,010
FILTRATE
328
DIGESTED SLUDGE
CAKE TO LAND FILL
PRIMARY DIGESTER
PRE-AERATION
PRIMARY SLUDGE 1,418
REAERATION
Δ -41
AERATION
Δ = 0
(3243)*
PRIMARY SETTLER
EFFLUENT
1,904
REAERATION
AERATION
428 WASTE SLUDGE
1 mgd RECYCLE
FINAL SETTLER
FINAL EFFLUENT
777

ESTIMATED RESERVOIRS OF NITROGEN	
AERATION UNITS	800 POUNDS†
DIGESTERS	2750 POUNDS

( )* indicates sum at this point

† multiply by 0.454 to obtain Kg

Figure 1. FIVE-DAY NITROGEN BALANCE: ARCHBOLD, OHIO. ALL VALUES IN POUNDS

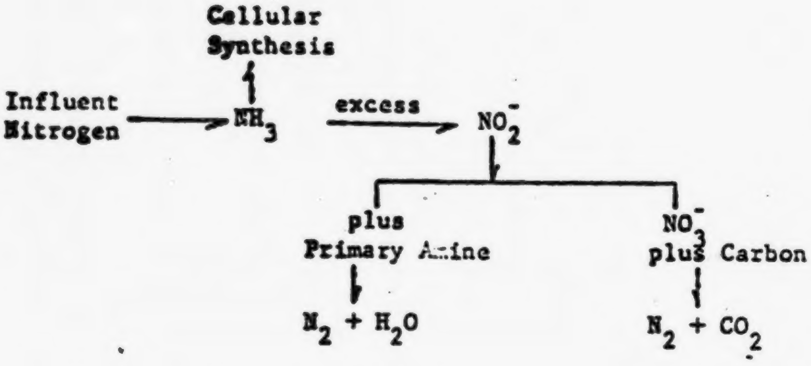
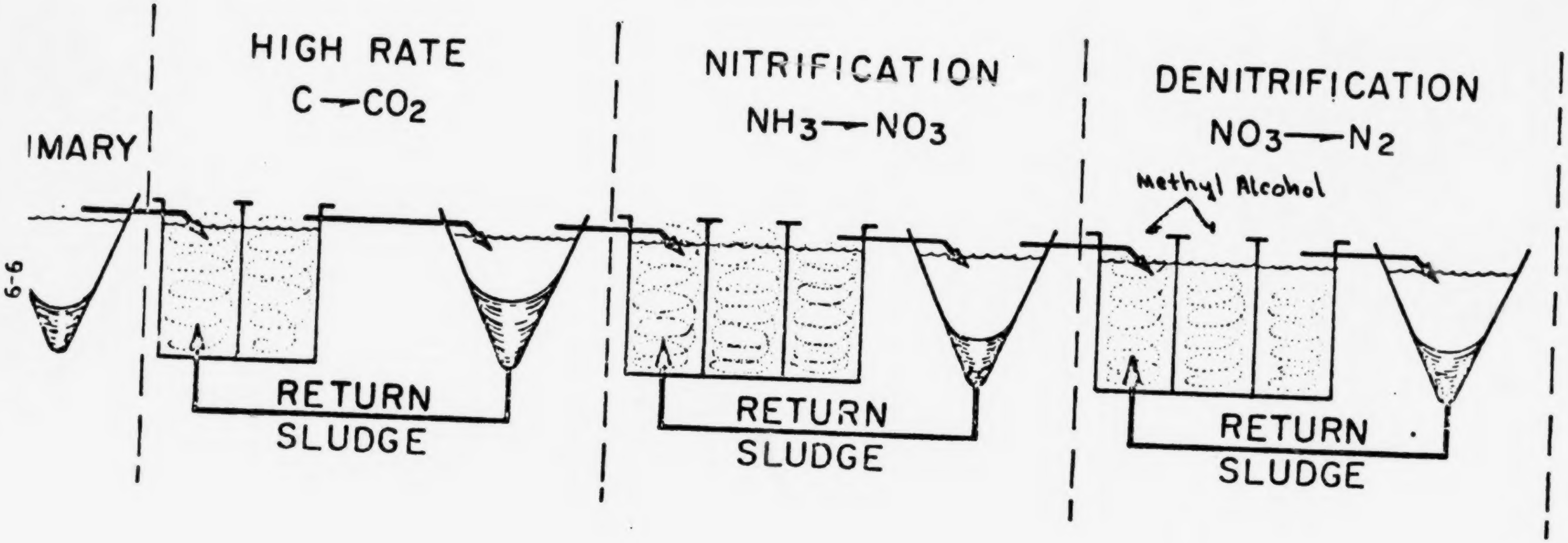

Cellular Synthesis
Influent Nitrogen
NH_3
excess
NO_2^-
plus Primary Amine
$N_2 + H_2O$
NO_3^- plus Carbon
$N_2 + CO_2$

FIGURE 1

FIGURE 5


IMARY
HIGH RATE
$C \rightarrow CO_2$
RETURN SLUDGE
NITRIFICATION
$NH_3 \rightarrow NO_3$
RETURN SLUDGE
DENITRIFICATION
$NO_3 \rightarrow N_2$
Methyl Alcohol
RETURN SLUDGE

OBJECTIVE

DEVISE TECHNIQUES FOR EFFICIENTLY REMOVING NITROGEN AND PHOSPHORUS FROM WASTEWATER COMPATIBLE WITH ACTIVATED SLUDGE TREATMENT.

APPROACH

1. UTILIZE THREE SEPARATE SLUDGE SYSTEMS TO ISOLATE SPECIFIC BIOLOGICAL ACTIVITIES, CARBON OXIDATION AND SYNTHESIS, NITRIFICATION, AND DENITRIFICATION.

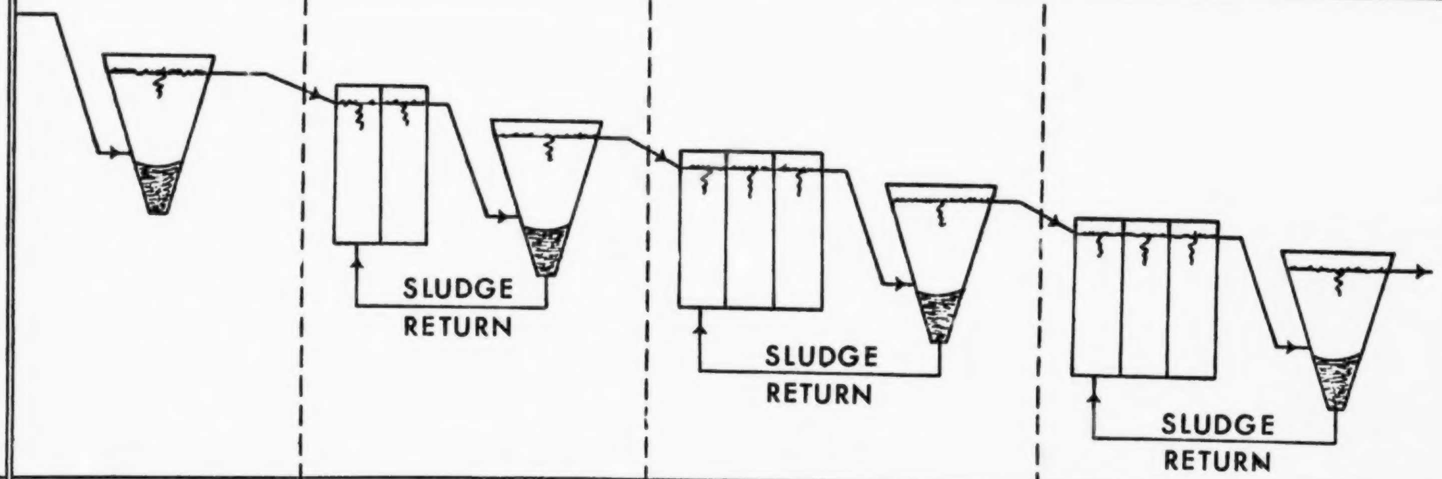
2. REMOVE BULK OF CARBON AHEAD OF NITROGEN CONTROL IN A HIGH-SYNTHESIS, SHORT DURATION MICROBIAL UNIT.

3. CONTROL NITRIFICATION AND DENITRIFICATION WITH ENRICHED CULTURES OF MICROORGANISMS.

4. SUPERIMPOSE CHEMICAL PRECIPITATION OF PHOSPHORUS ON THE THREE-STAGE NITROGEN CONTROL SYSTEM.

PROCESS FLOW DIAGRAM

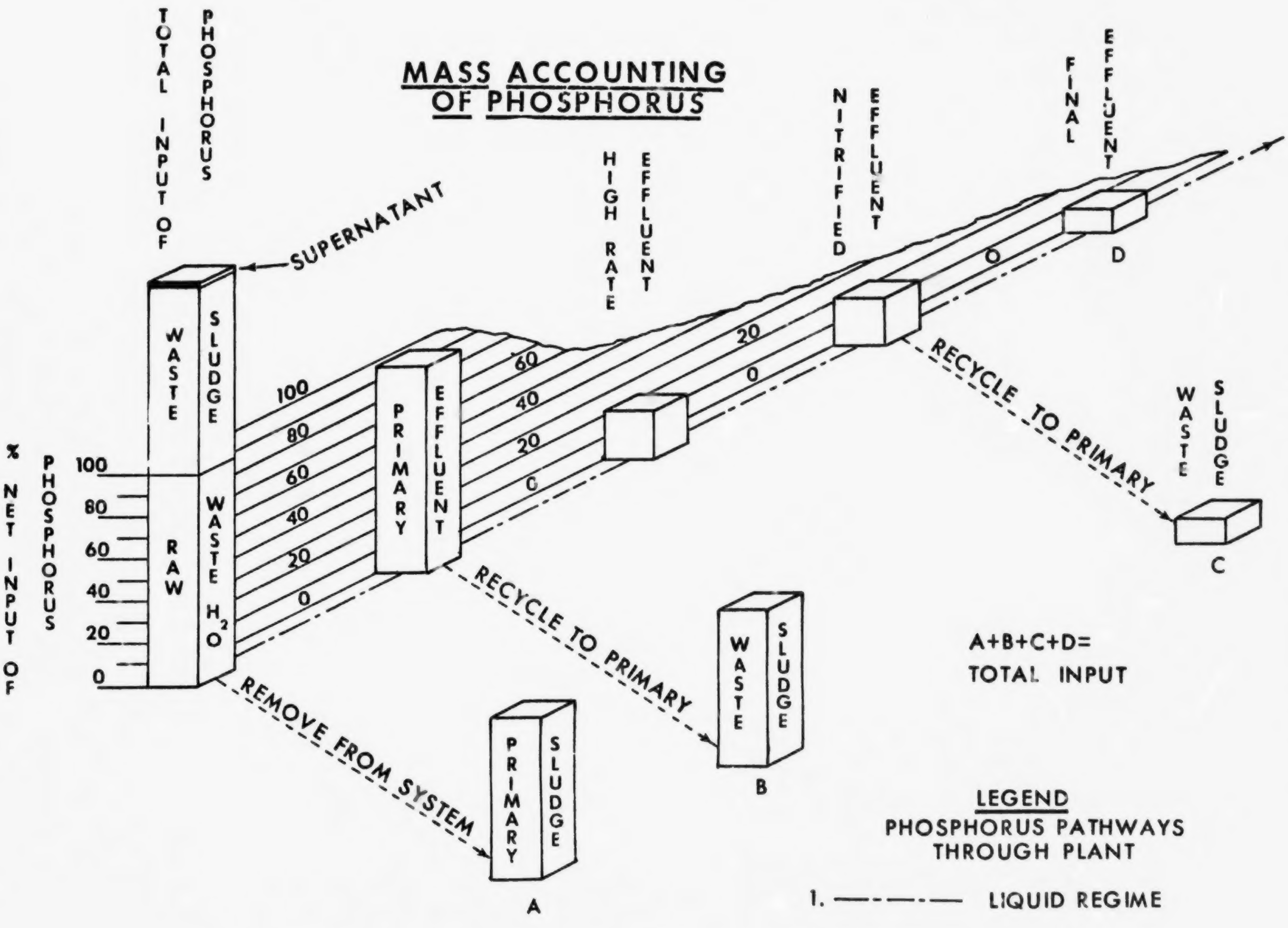
MAJOR PROCESS FUNCTIONS	REMOVE SETTLEABLE SOLIDS AND PARTICULATE COD	REMOVE BULK OF SOLUBLE ORGANICS AND PRECIPITATE PHOSPHORUS	CONVERT NH_3 TO NO_3	CONVERT NO_3 TO NITROGEN GAS AND CO_2 AND FURTHER REDUCE PHOSPHORUS
CHEMICAL ADDITIVES	NONE	SODIUM ALUMINATE	NONE	SODIUM ALUMINATE AND METHYL ALCOHOL
Unit	Primary	High—Rate	Nitrification	Denitrification


SLUDGE RETURN
SLUDGE RETURN
SLUDGE RETURN

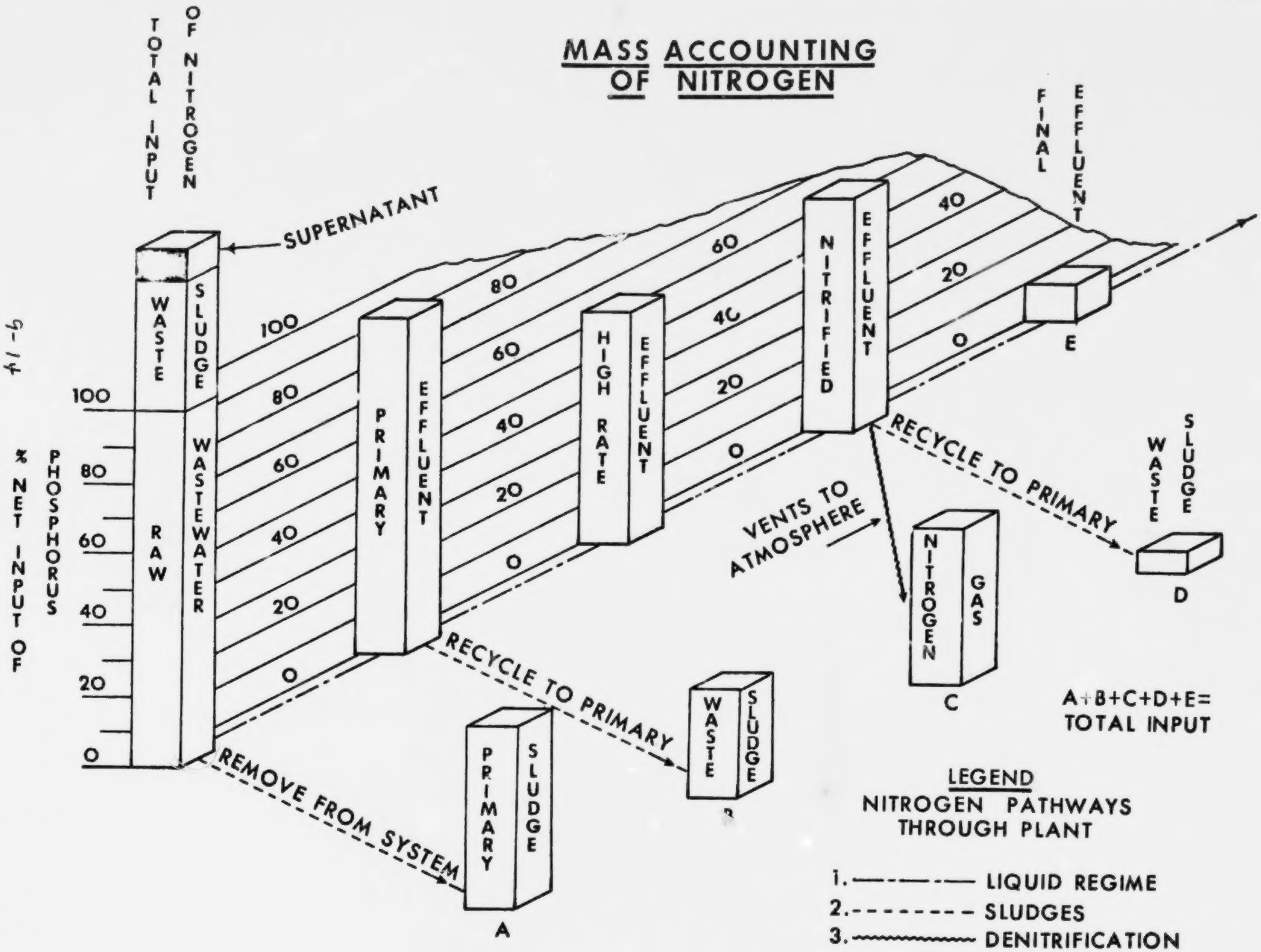
CHANGE IN COMPOSITION OF PROCESS STREAM DURING TREATMENT

PROCESS STREAM	mg/1							
	COD	S.S.	TOTAL P	ORG. N	NH_3 N	NO_2 N	NO_3 N	TOTAL N
RAW WASTEWATER	320	157	12.6	10.3 +	11.3 +	/	/ =	21.6
PRIMARY EFFLUENT	218	90	11.9	5.9 +	13.7 +	/	/ =	19.6
HIGH-RATE EFFLUENT	64	,9	2.8	0.8 +	7.7 +	1.1 +	4.3 =	13.9
NITRIFIED EFFLUENT	43	7	2.6	0.4 +	0.6 +	0.3 +	11.5 =	12.8
FINAL (DENITRIFIED) EFFLUENT	44	7	1.5	0.4 +	0.3 +	0.3 +	0.9 =	1.9
PERCENT (%) REMOVAL	86	95	88					91

MASS ACCOUNTING OF PHOSPHORUS


TOTAL INPUT OF PHOSPHORUS
% NET INPUT OF PHOSPHORUS
100
80
60
40
20
0
WASTE SLUDGE
RAW WASTE H2O
SUPERNATANT
PRIMARY EFFLUENT
HIGH RATE EFFLUENT
NITRIFIED EFFLUENT
FINAL EFFLUENT
REMOVE FROM SYSTEM
RECYCLE TO PRIMARY
RECYCLE TO PRIMARY
PRIMARY SLUDGE
A
WASTE SLUDGE
B
WASTE SLUDGE
C
D
A+B+C+D=
TOTAL INPUT
LEGEND
PHOSPHORUS PATHWAYS THROUGH PLANT
1. LIQUID REGIME
2. SLUDGES

MASS ACCOUNTING OF NITROGEN


TOTAL INPUT OF NITROGEN
% NET INPUT OF PHOSPHORUS
0
20
40
60
80
100
SUPERNATANT
WASTE SLUDGE
RAW WASTEWATER
100
80
60
40
20
0
PRIMARY EFFLUENT
80
60
40
20
0
HIGH RATE EFFLUENT
60
40
20
0
NITRIFIED EFFLUENT
40
20
0
FINAL EFFLUENT
E
REMOVE FROM SYSTEM
PRIMARY SLUDGE
A
RECYCLE TO PRIMARY
WASTE SLUDGE
B
VENTS TO ATMOSPHERE
NITROGEN GAS
C
RECYCLE TO PRIMARY
WASTE SLUDGE
D
A+B+C+D+E= TOTAL INPUT
LEGEND
NITROGEN PATHWAYS THROUGH PLANT
1. LIQUID REGIME
2. SLUDGES
3. DENITRIFICATION

MIXED LIQUOR CHARACTERISTICS AFTER ADDITION OF ALUMINUM

	Sludge Age days (Approx.)	MLSS mg/1	MLVSS mg/1	% Volatile	SDI	% Nitrogen V. S. Basis	% Phosphorus V. S. Basis	% Aluminum V. S. Basis
High-Rate Mixed Liquor	2	3,385	1,740	51	1.12	8.3	12.3	11.0
Nitrification Mixed Liquor	22	1,195	770	64	1.15	10.6	8.0	6.6
Denitrification Mixed Liquor	38	2,010	1,385	69	1.46	9.7	8.7	6.0

EFFECT OF ALUMINUM ON SLUDGES AND SUPERNATANT

1. HIGH-RATE MIXED LIQUOR CHARACTERISTICS

	MLSS mg/l	MLVSS mg/l	% VOLATILE	SDI	ORGANIC LOAD lb COD/day/ lb MLVSS
BEFORE Al^{+++}	1,450	900	62	0.44	2.6
AFTER Al^{+++}	3,385	1,740	51	1.12	1.6

2. PERCENT PHOSPHORUS IN SLUDGES - TOTAL SOLIDS BASIS

	PRIMARY	WASTE ACTIVATED	MIXED PRIMARY PLUS W. ACTIVATED	DIGESTED
BEFORE Al^{+++}	1.1	2.1	1.6	2.2
AFTER Al^{+++}	1.1	6.2	4.5	5.2

3. TOTAL PHOSPHORUS IN SUPERNATANT - mg/l

BEFORE Al^{+++}	170
AFTER Al^{+++}	60

CHEMICAL REQUIREMENTS AND COSTS

	Pilot Plant Data	Design Guideline
Phosphorus Concentration of Primary Effluent mg/l as P	12.2	10.0
Al to P ratio	1.5	1.2
Chemical Cost of Phosphorus Removal c/1000 gal	6.4	4.3
Nitrate Concentration of Nitrified Effluent mg/l as N	13.0	20.0
MeOH to NO_3-N ratio	5.8	4.0
Chemical Cost of Nitrogen Removal c/1000 gal	2.3	2.7
Total Chemical Cost c/1000 gal.	8.7	7.0

CHEMICAL APPROACHES TO NITROGEN REMOVAL

PH ADJUSTMENT OF EFFLUENT AND STRIPPING OF AMMONIA

FORMATION OF $MgNH_4PO_4$
  a) EFFLUENT
  b) DIGESTER SUPERNATANT

ADVANCED METHODS- ION EXCHANGE, ECT.

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PHYSICAL-CHEMICAL METHODS FOR NITROGEN REMOVAL

by

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Third Technical Session
9:45 A.M.
Thursday, February 6, 1969

Symposium on Nutrient Removal and Advanced Waste Treatment
Portland, Oregon

I. Nitrogen forms in secondary effluents. Neale '64, Barth '69.

  A. Ammonia-ammonium ions $NH_3 + H^+ \rightleftarrows NH_4^+$

    1. Av. 14, Range 0 to 36 mg/l as N.

    2. Derived from urea and other organic nitrogen in raw sewage.

    3. Suggested limit, 1 mg/l as N.

  B. Nitrite ions, NO_2^-.

    1. Av. 0.4, Range 0 to 10 mg/l as N.

    2. Produced from ammonia and CO_2 by Nitrosomonas bacteria when organic food is low.

    3. Suggested limit, 1 mg/l as N.

  C. Nitrate ions, NO_3^-.

    1. Av. 2.7, Range 0 to 25 mg/l as N.

    2. Produced from nitrite and CO_2 by Nitrobacter.

    3. PHS limit 10 mg/l as N (45 mg/l as NO_3^-).

  D. Ammonia-Nitrate are an either-or situation. Rare to get substantial quantities of both. Ammonia in high rate systems, nitrate with extended aeration.

II. Ammonia removal

A. Physical. Evaporation at high pH.

1. $NH_4^+ + OH^- \overset{pH\ 9.75}{\rightleftarrows} NH_3 + H_2O$

   90% as NH_3 at pH 10.75, 99% at pH 11.75.

2. Solubility. Very great compared with all ordinary gases.

   a. COMPARISON OF SOLUBILITY OF CARBON DIOXIDE AND NH_3 IN WATER

TEMP. (°C)	HENRY'S LAW CONSTANT (H)	
	CO_2	NH_3
20	1,420	0.7
40	2,330	1.8
60	3,410	3.8

WHERE $p_a = Hx_a$

Pa = VAPOR PRESSURE OF DISSOLVED SUBSTANCE "a" (atm)

x = MOLE FRACTION OF "a"

H = HENRY'S LAW CONSTANT

   b. 14 mg/l = .001 mole/55 moles water or .000018 mole fraction. Therefore P = 0.7 x .000018 Atm or .01 mm of Hg.

3. Air requirements compared to CO_2

a.

MINIMUM AIR REQUIREMENT FOR STRIPPING NH_3 AND CO_2 FROM WATER AT 20°C IN A COUNTERCURRENT OPERATION

	Stripping NH_3 out of basic solution*		Stripping CO_2 out of acidic solution*	
	NH_3 in water	NH_3 in air	CO_2 in water	CO_2 in air
	20 mg/l	↑ 8.7×10^{-6} g/g	20 mg/l	↑ 17.6×10^{-3} g/g
	2 mg/l ↓	0	2 mg/l ↓	0
Air Required:	225 cu ft/gal		0.11 cu ft/gal	

*Entering water stream and exiting air stream are assumed to be in equilibrium

b. Actual performance requires even more air--300 cu.ft./gal. for 90% removal determined at Tahoe. Slechta '67.

c. Temperature throughout most of the tower is wet bulb. This can be below zero degrees C in the winter and the tower will freeze. Henry's law constant is lower at low temperatures.

d. Packed towers have prohibitive pressure drops.
38 inches of water in Intalox packing.
Fraction of an inch in cooling tower.

B. Ion exchange as NH_4^+ at pH's below 8

1. Adsorption. R^- is a cation exchange material.

   a. $R^-Na^+ + NH_4^+ \rightleftharpoons R^-NH_4^+ + Na^+$

   b. $R_2^-Ca^{++} + 2\ NH_4^+ \rightleftharpoons 2R^-NH_4^+ + Ca^{++}$

2. Regeneration

   a. Reverse of 1 using excess salt or

   b. $R^-NH_4^+ + Na^+OH^- \longrightarrow R^-Na^+ + NH_3 + H_2O$

   $2R^-NH_4^+ + Ca(OH)_2 \longrightarrow R_2^-Ca^{++} + 2NH_3 + 2H_2O$

   Displacement of NH_3 with base.

3. Specificity

   a. Ion exchange resins favor Ca^{++} over NH_4^+. Hardness of water uses up available capacity.

   b. Some zeolites favor NH_4^+ or Ca^{++}. Clinoptilolite. Battelle-Northwest. Ames '68. Figures 1 and 2.

4. **Adsorption. Conventional** ion exchange equipment. Packed towers up or downflow.

5. Regeneration

   a. Conventional resins with brine.
   b. Specific zeolites with base. Lime can precipitate calcium carbonate in zeolite.

6. Disposal

   a. To ocean. Brines.
   b. To air by lime treatment and blowing.

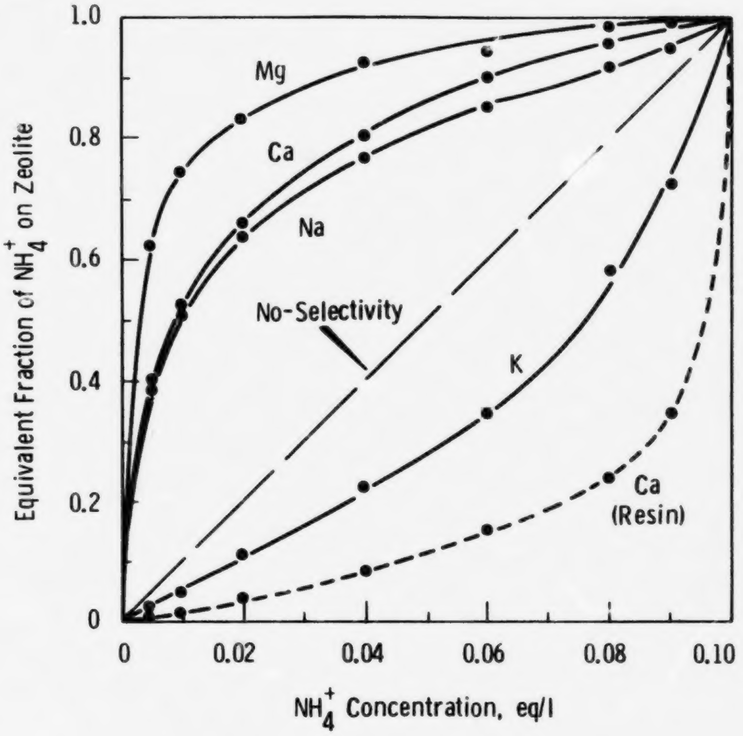


FIGURE 1. The 23°C ion Exchange Isotherms for the Reaction of NH_4^+ with Na^+, K^+, Mg^{+2}, and Ca^{+2} for Hector Clinoptilolite and the Reaction NH_4^+ with Ca^{+2} for a Polystyrene Sulfonate ion Exchange Resin. Total Solution Normality was Constant at 0.1 for all Systems.

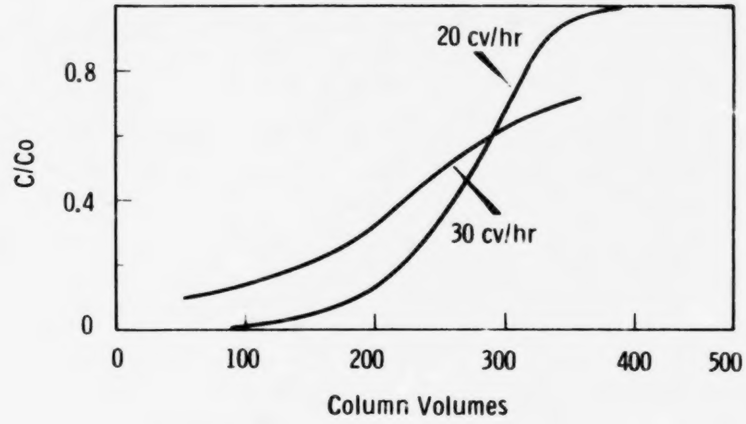


FIGURE 2. Effect of Flow Rate on Uptake of NH_4^+

Column	35 cc of 25 x 50 Mesh Clinoptilolite
Feed	Simulated Clarified Secondary Effluent
C/Co	$\frac{\text{Effluent } NH_4^+ \text{ Concentration}}{\text{Influent } NH_4^+ \text{ Concentration}}$

C. Chemical destruction

1. Chlorine

   a. $3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$

   b. $NH_3 \xrightarrow{Cl_2} NH_2Cl \xrightarrow{Cl_2} NHCl_2 \xrightarrow{Cl_2} NCl_3$

   c. Requires from 6.25 up to 10 mg Cl_2 per mg ammonia N.

2. Ozone

   $NH_3 + O_3 + OH^- \longrightarrow NO_3^- + 2H_2O + 4O_2$
   Not efficient at low concentrations.
   Converts NH_3 limit 1 mg/l into NO_3^- limit 10 mg/l.

III. Nitrate removal

A. Ion exchange. $R^+NO_3^-$

1. Conventional. Competition from Cl^-, HCO_3^-, and especially $SO_4^=$ and $HPO_4^=$.

2. Specific resins. Research being carried out.

   a. Most resins show some specificity for NO_3^- but low selectivity versus $SO_4^=$.

B. Chemical reduction. Rocketdyne

1. $2NO_3^- + 15FeSO_4 + 34H_2O \xrightarrow{Cu^{++}}$

   $5Fe^{++}Fe_2^{+++}(OH^-)_8\downarrow + N_2 + 14H_2SO_4 + SO_4^=$

2. $2NO_3^- + 24FeSO_4 + 58H_2O \xrightarrow{Cu^{++}}$

   $8Fe^{++}Fe_2^{+++}(OH)_8\downarrow + 2NH_4^+ + SO_4^= + 11H_2SO_4$

   a. Reactions 1 and 2 can go in about equal proportions.

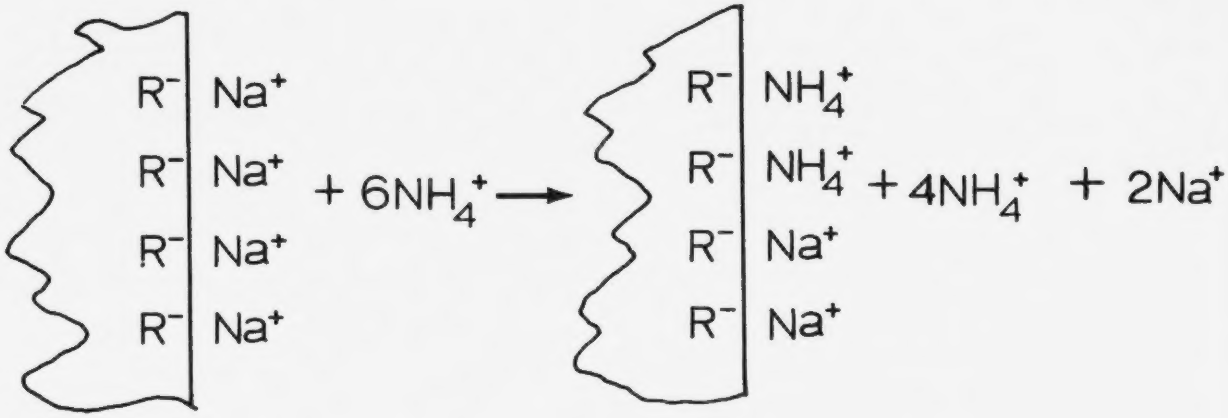
   b. $FeSO_4 \cdot 7H_2O$ "copperas" is cheap but there is a lot of precipitate of black iron hydroxides and sulfates.

   c. Utility limited to availability of ferrous salts at low cost and convenient dump for precipitates.

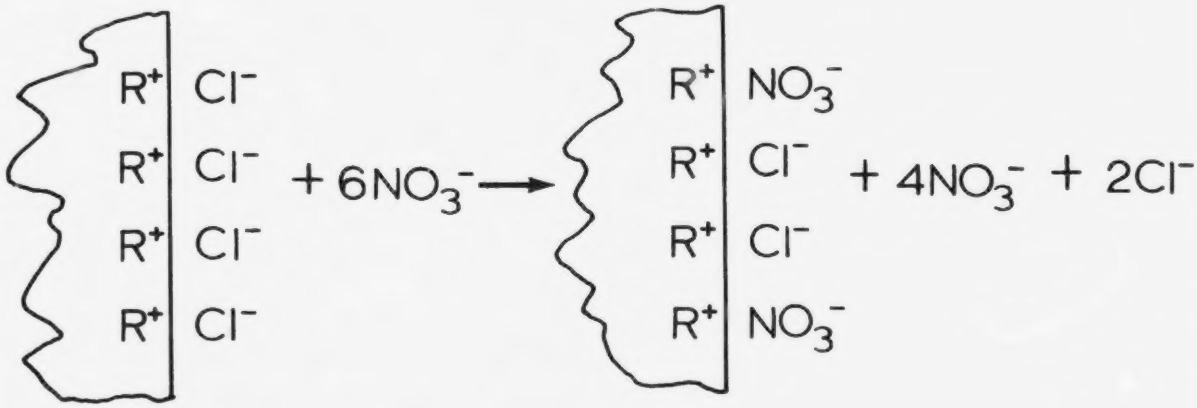
   d. Useful in situations where neither denitrification nor ammonia stripping can be used. Toxic chemical wastes and low temperature part time operations.

REMOVAL OF IONS BY ION-EXCHANGE RESINS

Cation-Exchange Resin


R^- Na^+
R^- Na^+
R^- Na^+
R^- Na^+
$+ 6NH_4^+ \rightarrow$
R^- NH_4^+
R^- NH_4^+
R^- Na^+
R^- Na^+
$+ 4NH_4^+ + 2Na^+$

Anion-Exchange Resin


R^+ Cl^-
R^+ Cl^-
R^+ Cl^-
R^+ Cl^-
$+ 6NO_3^- \rightarrow$
R^+ NO_3^-
R^+ Cl^-
R^+ Cl^-
R^+ NO_3^-
$+ 4NO_3^- + 2Cl^-$

IV. Cost of reducing nitrogen from 20 to 2 mg/l. ¢/1000 gal. Slechta. 10 MGD basis.

A. As ammonia

1. Stripping at high pH.

a. 2.3¢ at pH 11 adjusted for cold weather operation.
b. 4.9¢ including cost of lime to raise pH.
Lime cost can be shared with phosphate removal.
c. Cost is not sensitive to fluctuation in actual nitrogen quantities.

2. Chlorine

a. 5.3¢
b. Cost directly related to actual NH_3 quantity.

3. Ion exchange

a. Non-specific resin 8.1¢. Eliassen.
b. Zeolite. Unknown.
c. Costs strongly dependent on actual quantity treated.

B. As nitrate. No costs assigned to excess aeration required to achieve nitrification.

1. Ion exchange

a. Non-specific resin 18.0¢.

2. Chemical reduction by ferrous sulfate

a. 8.6¢ not including sludge disposal. Unpublished.

3. Biological reduction

a. 2.7¢. Barth.

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SOLIDS REMOVAL PROCESSES

by

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Technical Seminar
Nutrient Removal and Advanced
Waste Treatment
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November 13-14, 1968

Solids Removal

J. J. Convery

I. Screening Devices*

A. Functional Description

Microscreening is a form of simple filtration. These mechanical filters consist of a rotary drum which revolves on a horizontal axis. The peripheral surface of the drum is covered with a stainless steel filter fabric. The effectiveness of the woven mesh screen for retaining fine particles is dependent on the size of openings in the screen and on the pattern of the weave employed. Influent enters the open end of the drum and is filtered through the fabric with the intercepted solids being retained on the inside surface of the fabric. As the drum rotates, the solids are transported and continuously removed at the top of the drum by pumping strained effluent, under pressure, through a series of spray nozzles which extend the length of the drum. The solids and wash water are collected in a central trough within the drum and discharged through a hollow axle. Some mechanism such as intermittent chlorination (every 3 to 8 days), or continuous ultraviolet lighting must be employed to prevent the growth of biological slimes on the fabric.

B. Physical Description

A typical microstraining unit is shown in Figure 1.

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*Comments and operating experience refer to the patented Micro-Strainer, a product of Glenfield and Kennedy, Ltd., London, England. Mention of a proprietary name is not an endorsement by FWPCA.

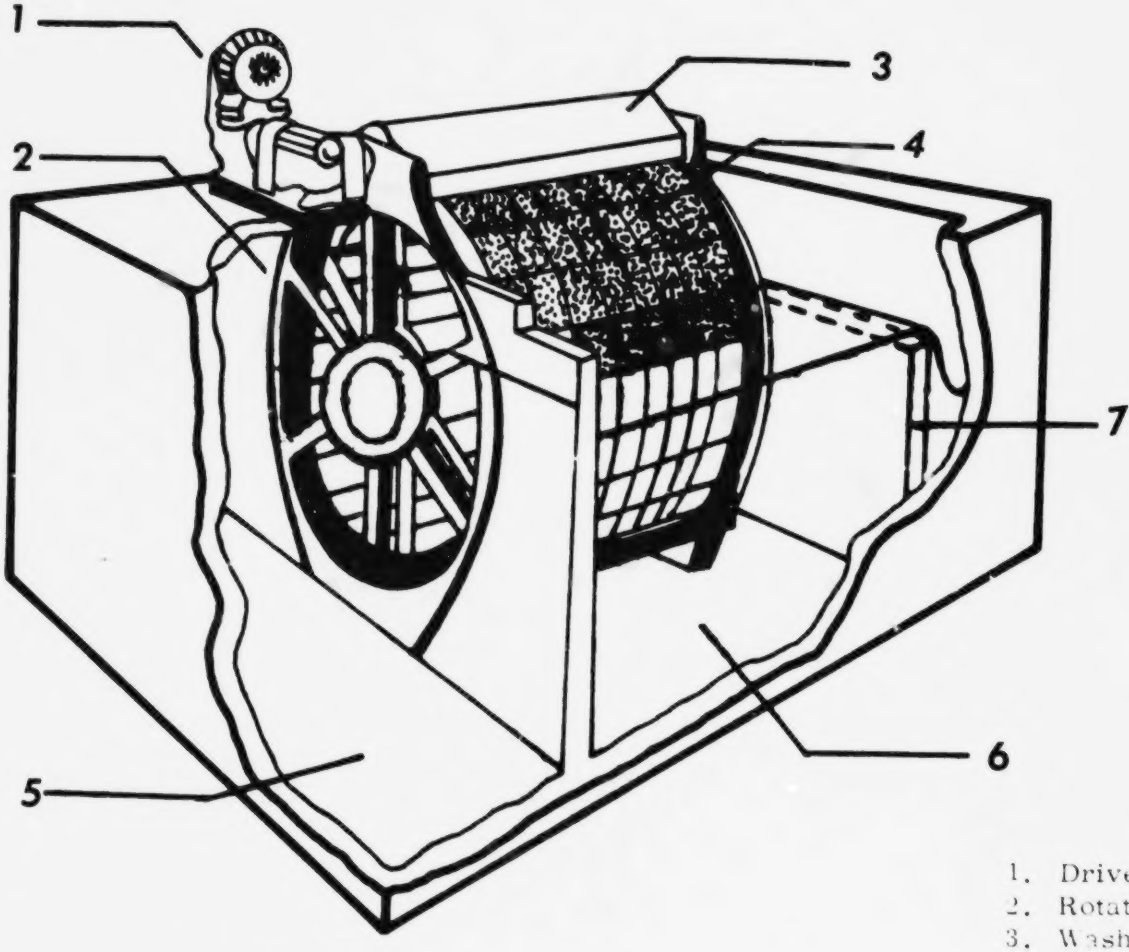


Fig. 1 Typical Microstrainer Unit

1. Drive Unit
2. Rotating Drum
3. Wash-water Jets
4. Micro-fabric
5. Influent Chamber
6. Effluent Chamber
7. Effluent Weir

Not Shown

Wastewater Hopper
Ultra-violet Lamp
Wash-water Pump

1. Unit Sizes and Capacity[8]

Drum Sizes in Feet		Approx. Capacity mgd
Diameter	Width	
5	1	0.05 - 0.5
5	3	0.3 - 1.5
7½	5	0.8 - 4
10	10	3 - 10

2. Fabric Details
See Table 1

C. Design Basis

The basic design criteria for the proper sizing of a microscreening unit is the filterability index, I. A device called the filtrameter[1] is available from Glenfield and Kennedy, Inc. for the field measurement of the filterability index I. This index is an expression of the volume of water obtained per unit headloss when passed at a standard rate through a unit area of standard filter fabric. The index is used to calculate the required area to treat a given flow of a specific wastewater according to the following expression:

$$H = \frac{mQC_f e^{nIQ/S}}{A}$$

where:

H = headloss, in.
Q = rate of flow, gpm
C_f = initial fabric resistance, sec.
A = effective submerged filter area, ft^2
I = filterability index, ft^{-1}
S = speed of rotation, area per unit time entering the water, ft^2/min.

The unit conversion factors m and n have values of 0.0267 and 0.1337, respectively. C_f is 1.8 sec. for the Mark 0 fabric and 1.0 sec. for the Mark I fabric.

TABLE 1

CHARACTERISTICS OF THREE FILTER FABRICS

	Mark 0	Mark I	Mark II
Apertures:	1/1000 23 microns	1.5/1000 35 microns	2.5/1000 60 microns
No. per sq. in.:	160,000	80,000	60,000
No. per lineal in.:	400	280	240
Warp:	120 mesh 2 wires .0018	76 mesh 2 wires .0024	60 mesh 2 wires .0040
Weft:	600 mesh 1 wire .0016	500 mesh 1 wire .0022	420 mesh 1 wire .0028

D. Operating Parameters

1. Headloss

Microscreening devices should be installed at an elevation permitting gravity flow thereby eliminating the possible fractionation of flocculant particles. Experience has demonstrated that the removal efficiency of particulates is reduced when flocculant material is pumped.[2] The maximum operating headloss across the screen is normally limited to six (6) inches to prevent rupture of the delicate filter fabric.

2. Drum Speed

Some flexibility of operation can be achieved by varying the speed of rotation, S. Peripheral velocities normally range from 25 to 135 ft/min.

3. Wash Water Requirements

The function of backwashing is to thoroughly clean the filter fabric during each revolution with a minimum of wash water. Pressure appears to be more critical than the quantity of wash water to effect the cleaning. Wash water pressures range from 20 to 55 psi and water requirements are less than 5% of the throughput. The wash water is normally recirculated to the head end of the plant. The suspended solids concentration of the wash water approach 750 mg/l.

E. Performance in a Tertiary Treatment Application

1. Removal Efficiency and Flow Rate[8]

The effect of aperture size on removal efficiencies and flow rate are shown in the following table:

Fabric	Removal Solids	Efficiency BOD	Flow Gals./Hr/Ft^2
Mark O (23 microns)	70-80%	60-70%	400
Mark I (35 microns)	50-60%	40-50%	600

2. Operating Problems

The Federal Water Pollution Control Administration has conducted a study[3] of microscreening at Lebanon, Ohio. The secondary effluent from the municipal activated sludge treatment plant had an average suspended solids concentration of 17 mg/l while the Mark O fabric was tested and 27 mg/l during tests of the Mark I fabric. The filterability index, coincidentally, was 17.0 during both tests.

One of the major problems associated with operation of the microscreen was the unit's inability to handle wide fluctuations in solids loadings. On one occasion the solids in the feed increased 8 fold from 25 to 200 mg/l. Within minutes the throughput of the unit was reduced from 60 to 13 gpm (21.7% of rated capacity). Figure 2 shows a frequency distribution of suspended solids values in the Lebanon secondary effluent.

Suspended solids concentrations in excess of 50 mg/l occurred 10% of the time. If the microscreening unit can produce 25% of its rated capacity during periods of high solids loading, (> 50 mg/l) 75% of the design flow must come from storage 10% of the time. Therefore, the plant must have an excess design capacity of 8.33%. A recent design improvement has been the coordination of drum speed and wash water pressure with changes in headloss across the fabric.

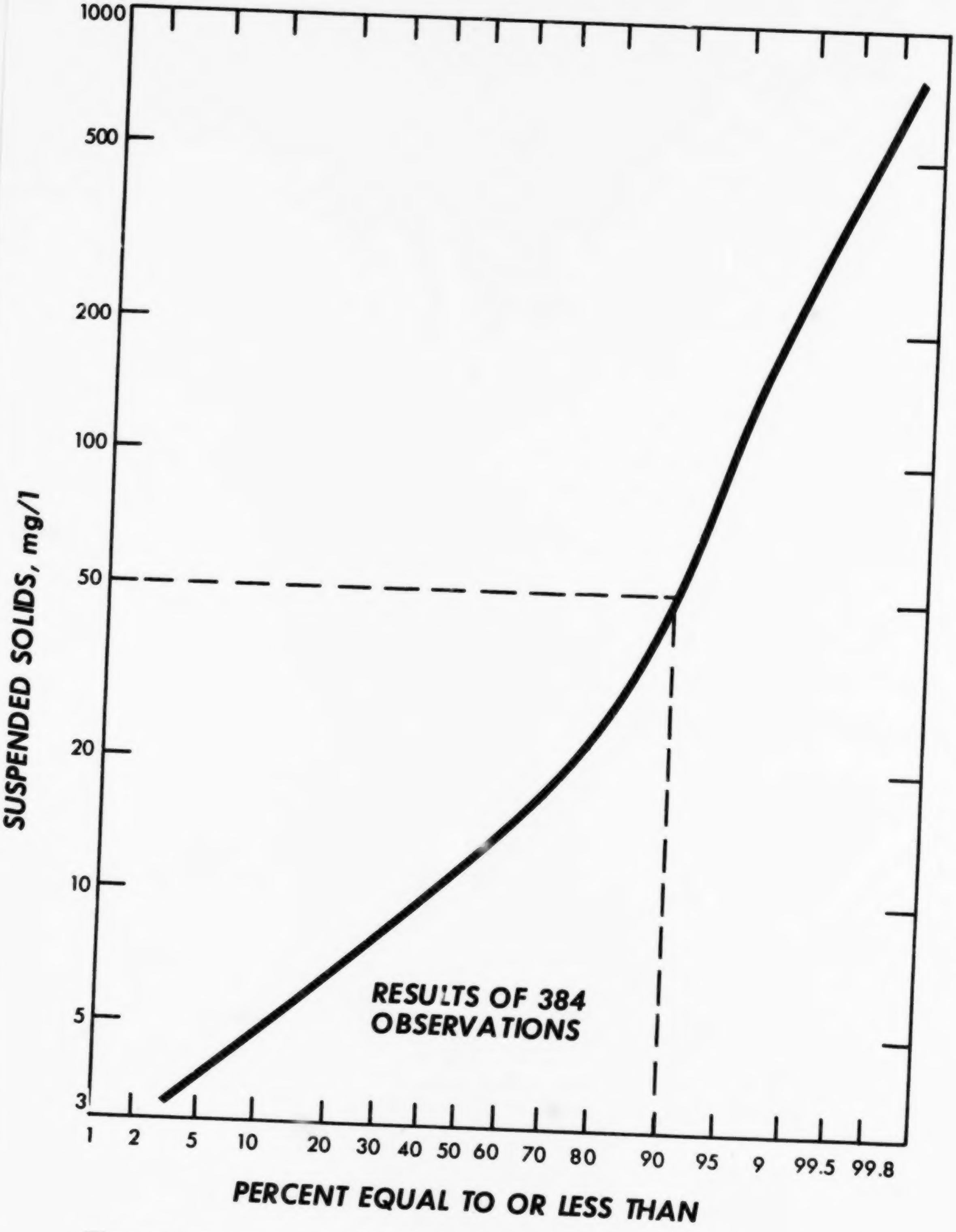


Figure 2. Frequency distribution of suspended solids in secondary effluent.

3. Limitations

Fine fabric microscreening is not recommended for the treatment of waters with a chloride content greater than 500 mg/l because of potential corrosion problems.

F. Capital and Operating Costs

The capital and operating costs associated with microstraining of secondary effluent have been prepared by Smith[10] and are shown in Figure 3.

II. Coarse Media Upflow Filtration[9]

The work on upflow filtration, which I have summarized, was a 12-month study performed by Truesdale and Birkbeck at Letchworth, England in 1967.

A. Description

The upflow coarse media filter is somewhat similar in appearance to the conventional rapid sand filter except that the direction of flow is upward. Backwashing in an upward direction grades the filter media with the coarser media on the bottom and finer media on the top. During filtration the effluent contacts progressively finer media and the intercepted solids are distributed throughout the filter bed rather than being concentrated near the surface. This uniform distribution of headloss and successively finer filtration are the reasons for the longer filter runs and improved product quality normally associated with in-depth filtration.

Upflow coarse media filters consist of 5 feet of 1-2 mm sand supported on progressively coarser layers of gravel and a distribution system. Total height is approximately 12 feet. A metal grid, consisting of parallel bars spaced 4 in. apart placed 2 in. below the surface of the bed, is used to prevent expansion of the filter media at flow rates as high as 6.7 gpm/ft^2. The backwash rate of 11.7 gpm/ft^2 is sufficient to expand the bed to permit cleaning. A wash cycle of 15 minutes was found adequate to clean the filter.

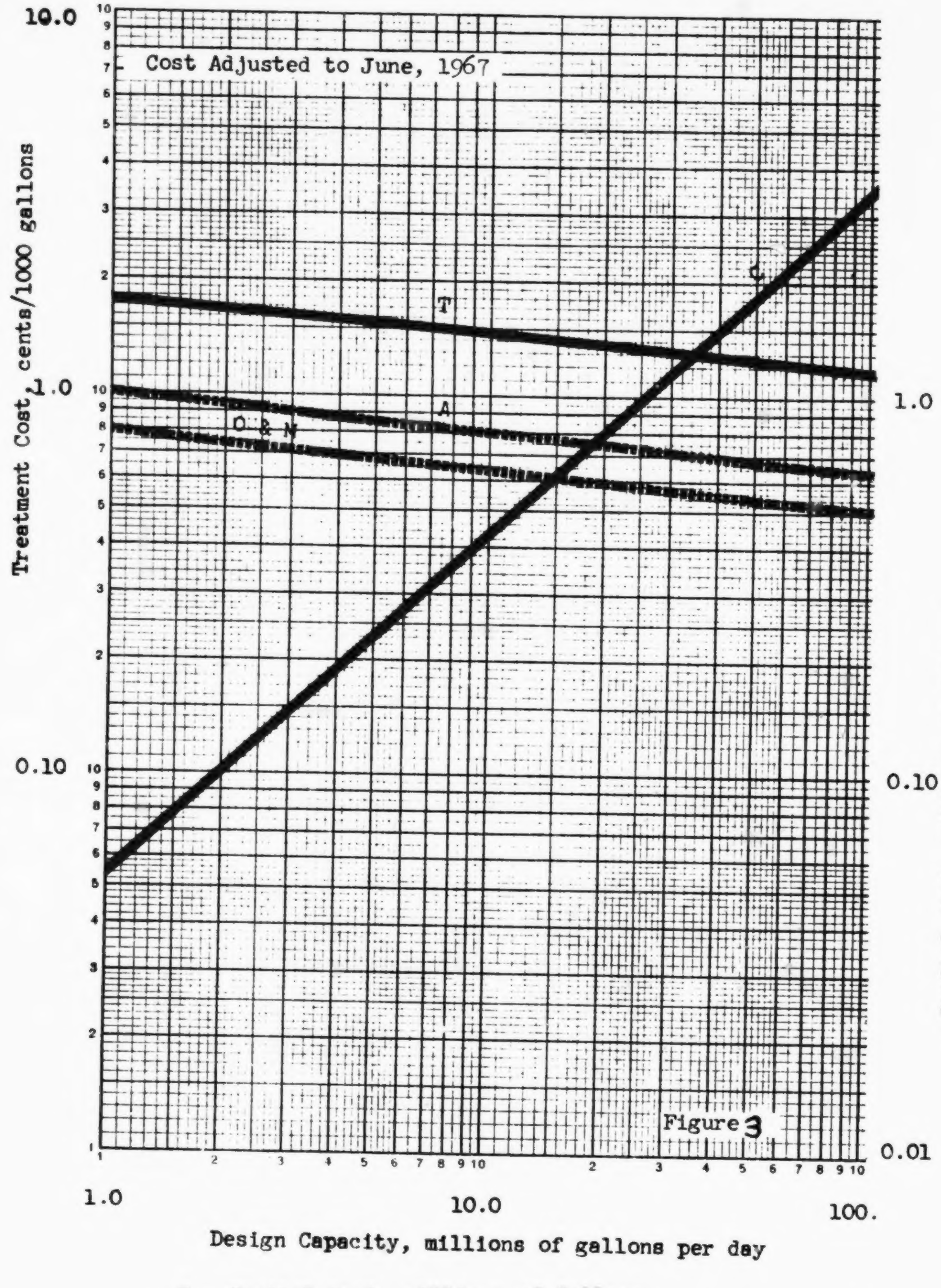
B. Performance

The solids concentration of the activated sludge effluent varied from 10 to 34 mg/l. The effluent from the upflow coarse media

Figure 3

MICROSTRAINING OF SECONDARY EFFLUENT

Capital Cost, Operating & Maintenance Cost, Debt Service
vs.
Design Capacity



C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons(4 1/2% - 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

filter contained from 3.2 to 10 mg/l of suspended solids. The coarse media filter removed on the average 60% of the suspended solids and 53% of the BOD. The removal efficiency of a filter is a function of the hydraulic loading as shown in the following table:

Filtration Rate gpm/ft^2	Solids Removal Efficiency %
2.9	77
4.1	58
5.9	38

The longest length of run was 19.2 hours at a filtration rate of 3.3 gpm/ft^2. Wash water consumption ranged from 4.6 to 6.7 percent of the filter throughput. The authors did not mention what terminal headloss was used to initiate the automatic backwash mechanism but they do indicate it was set too low. Therefore, extended filter runs and lower wash water consumption may be obtainable.

A microstraining unit with a Mark O fabric was operated in parallel with the upflow filter during this study. Results indicated that the filter effluent was superior to the strainer effluent at a filtration rate of 3.33 gpm/ft^2 or less. Filter performance was inferior to strainer performance at a filtration rate of 6.67 gpm/ft^2 or more. Performance was comparable at the intermediate filtration rates of 3.33 to 6.67 gpm/ft^2. The microstrainer was operated at 4.3 gpm/ft^2.

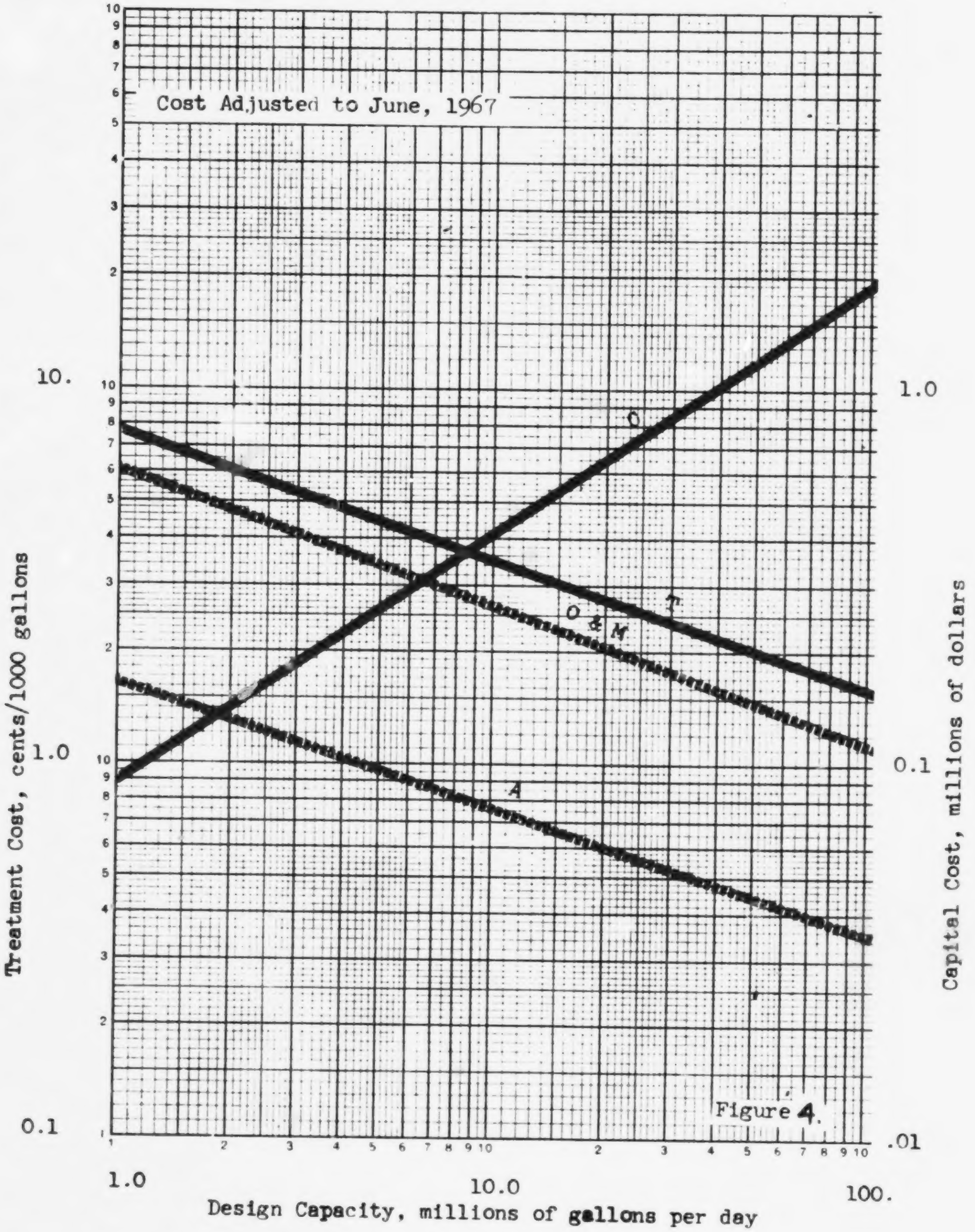
One advantage of coarse media filtration is the availability of some floc storage capacity within the interstices of the filter media to permit partial phosphorus removal by chemical pretreatment. The practice of chemical pretreatment prior to microstraining has generally not been successful. The fragile floc breaks up on the screen.

The capital and operating costs for filtration through sand or graded media at 4 gpm/ft^2 has been estimated by Smith[10] and are shown in Figure 4.

Figure 4

FILTRATION THROUGH SAND OR GRADED MEDIA - 4GPM/SQ FT

Capital Cost, Operating & Maintenance Cost, Debt Service
vs.
Design Capacity



C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons(4 1/2% - 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

III. Moving Bed Filter Technique

A. Description

The Moving Bed Filter (MBF) is a new filtering technique that is currently being developed by Johns-Manville Products Corporation.* Evaluation of a pilot unit is currently being supported under contract by the FWPCA. A schematic diagram of the Moving Bed Filter is shown in Figure 5.

This unit is basically a sand filter. Particulate matter in the water is removed as the water passes through the sand (.6 - .8 mm). As the filter surface becomes clogged, the filter media is moved forward by means of a mechanical diaphragm. The clogged filter surface is guillotined off thereby exposing a clean filter surface. The sand and accumulated sludge is washed and the sand is returned to the base of the filter. The unit is thus a form of countercurrent extraction device feeding sand countercurrent to the water being filtered. The Moving Bed Filter has a renewable filter surface analogous to the microstrainer and the advantage of depth filtration comparable to the coarse media filter. The unit does not have to be taken off stream for backwashing. In theory, 1% of the filter is being backwashed 100% of the time compared to the conventional practice of backwashing 100% of the filter 1% of the time.

B. Performance

Several pilot MBF units have been built to date and used to treat settled and unsettled trickling filter effluent and primary effluent. The system lends itself well to the use of chemical aids ahead of filtration because of designed flexibility to handle high solids loadings.

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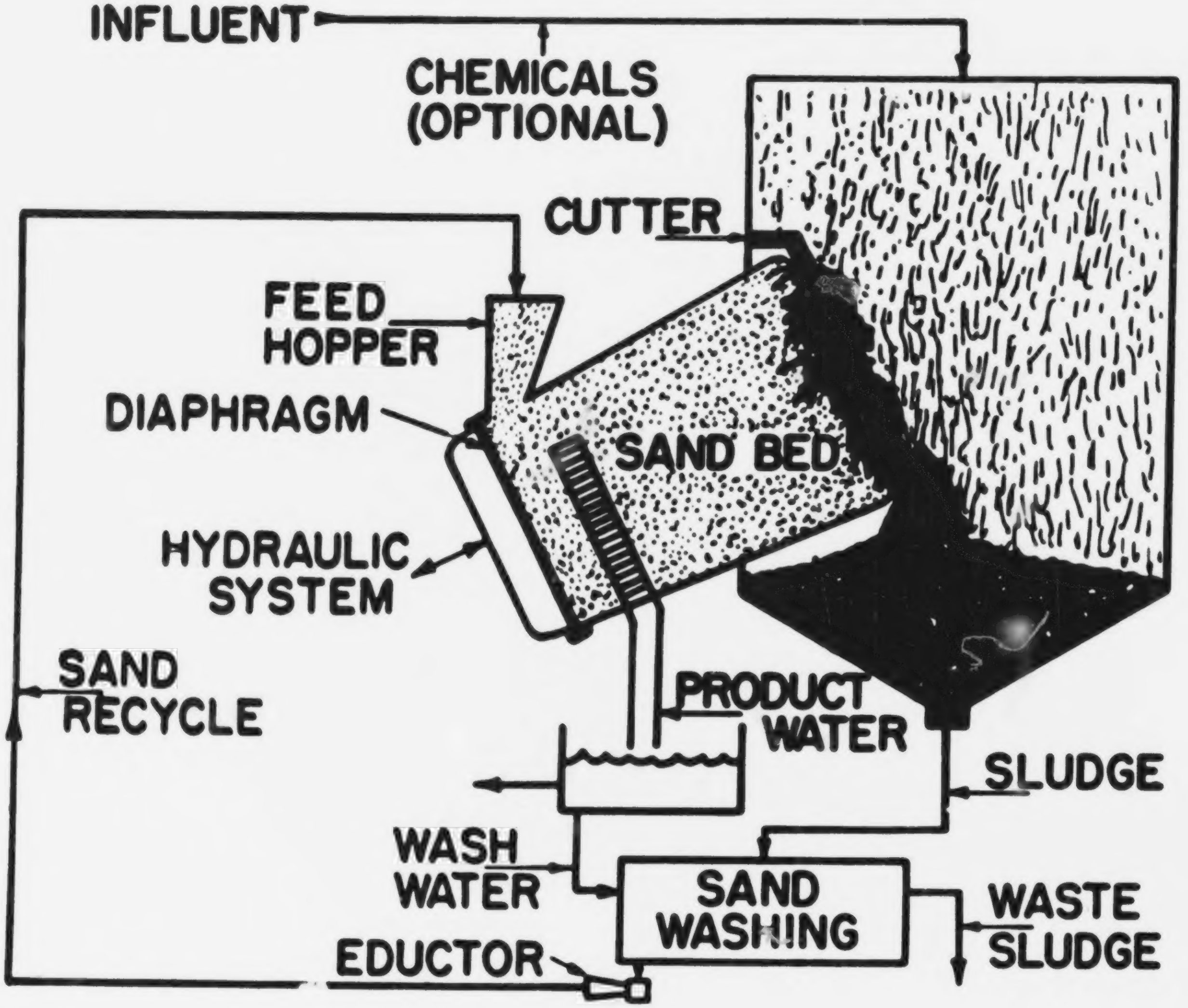
*Mention of a proprietary device does not indicate endorsement by the FWPCA.

FIGURE 5

BASIC CONCEPT OF MOVING BED FILTER


INFLUENT
CHEMICALS (OPTIONAL)
CUTTER
FEED HOPPER
DIAPHRAGM
SAND BED
HYDRAULIC SYSTEM
SAND RECYCLE
PRODUCT WATER
SLUDGE
WASH WATER
SAND WASHING
WASTE SLUDGE
EDUCTOR

Preliminary results obtained while treating unsettled trickling filter effluent are as follows:

ALUM DOSE mg/l	COAG. AID mg/l	TURBIDITY JTU			BOD mg/l			COD mg/l			TOTAL PHOSPHATE mg/l		
		Inf.	Eff.	% Red.	Inf.	Eff.	% Red.	Inf.	Eff.	% Red.	Inf.	Eff.	% Red.
200	0	41	10.0	76	40	8.8	78	120	40	66	36	1.5	96
200	0.5	40	6.3	85	49	9.7	80	143	39	73	36	2.5	93
200	1.0	22	9.2	57	46	10.0	79	111	42	62	40	1.8	96
100	0.5	28	8.4	64	64	9.7	79	172	43	65	30	1.7	94

These very preliminary results look encouraging. Of particular interest is the excellent phosphate removal obtained with 100 mg/l of alum. This represents an AL/P ratio of about 1. We are following this relationship very closely.

It is too premature to even suggest a treatment cost for the Moving Bed Filter. Design and performance information developed from the Johns-Manville-FWPCA contract will be analyzed to project capital and O&M costs for comparison with alternate treatment processes.

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ORGANIC RESIDUE REMOVAL

by

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Technical Seminar
Nutrient Removal and Advanced
Waste Treatment
Portland, Oregon
February 5 and 6, 1969

USE OF GRANULAR ACTIVATED CARBON

I INTRODUCTION

A Figure 1 shows the predicted water use and water supply picture through the year 2000. This is a national picture -- in some areas, demand already exceeds supply and population, industrial and economic growth are limited. This graph does not allow for reuse so the situation is not as dark as indicated.

B This Nation's usable water supply must be increased -- potential solutions are desalting of sea water, weather control, building of reservoirs, and wastewater renovation. All approaches should be investigated thoroughly because of immense burden that water shortages can place on well-being of citizens.

C Before wastewater can be reused for potable purposes, we must remove objectionable contaminants added by use. Table 1 lists the organic materials added to a municipal water supply by one use and not removed by conventional (activated sludge) treatment.

D These refractory organic materials must be removed to a greater degree than is done now whether the water is directly reused or returned to a stream. Figure 2 shows the projected input of organic materials as measured by chemical oxygen demand (COD) through the year 2000. Most of these organics are dissolved rather than suspended solids. Since these COD materials are, for the most part, resistant to biological treatment, their concentration will not be affected by widespread application of the activated sludge process (solid line). An efficient organic removal process is needed to reduce the input to that shown by the dotted line. These materials, if put into a stream, promote algal growth, contribute to fish kills and tainting of fish flesh and to taste and odor of water supplies withdrawn from the river. In addition, there is a possibility that they will have cumulative harmful physiological effects.

E Processes that have been and are being considered for removal of these organic materials include distillation, freezing, reverse osmosis and adsorption on activated carbon, both granular and powdered.

F Adsorption on granular carbon is the farthest advanced of these processes. Already in commercial use for wastewater treatment, the technology is ready for use on a large scale. This outline considers the "State of the Art" of carbon use.

II THE MANUFACTURING OF ACTIVATED CARBON

A Source materials include coal, wood, sawdust, peat, lignite and pulp mill char.

B In the first step of manufacturing, the raw material is carbonized in the absence of air, usually below 600°C. This step removes the bulk of the volatile materials and yields a product with slightly enhanced adsorptive capacity.

1 Carbonization is sometimes made more efficient by the addition of metallic chlorides (zinc chloride is common) to the carbonaceous material before heating. The heating is continued until zinc chloride vapors come off, after which the char is cooled and washed to recover the zinc salt for reuse.

C Activation is controlled oxidation at elevated temperatures. Activation gases are usually steam or carbon dioxide and the temperature is held between 800 and 1000°C. The time of activation varies between 30 minutes and 24 hours, depending on the oxidizing conditions and on the quality of active carbon desired.

The major manufacturers of activated carbon are listed below, in alphabetical order:

1 Granular

American Norit Company, Inc.
Atlas Chemical Industries, Inc.
National Carbon Company
Pittsburgh Activated Carbon Co.
(Calgon Corporation)
West Virginia Pulp and Paper Co.
Witco Chemical Company, Inc.

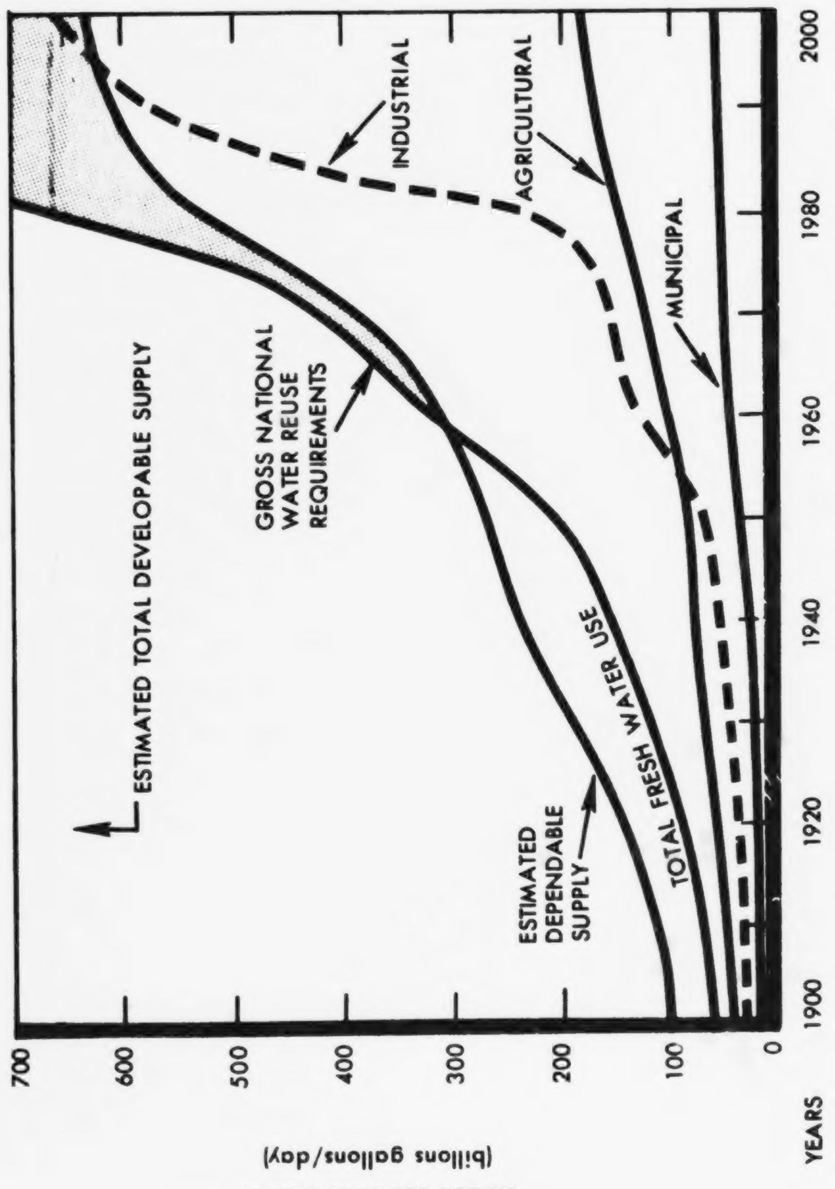


Figure 1. WATER USE AND WATER SUPPLY IN THE UNITED STATES (1900-2000)

Table I

EXAMPLES OF ORGANIC MATERIALS REMAINING IN SECONDARY EFFLUENT

- TANNINS
- LIGNINS
- ETHERS
- ALKYLBENZENESULFONATE
- SUBSTITUTED BENZENE INSECTICIDES
- PROTEINACEOUS MATERIAL
- END PRODUCTS OF BIOLOGICAL OXIDATION

2 Powdered

American Norit Company, Inc.
Atlas Chemical Industries, Inc.
West Virginia Pulp & Paper Company

III PRINCIPLES OF ADSORPTION ON GRANULAR CARBON IN COLUMNS

A Adsorption is a phenomenon by which solutes in a solution are attracted to and adhere to the surface of solid materials. Activated carbon is a particularly good adsorbent because it has an extremely large surface area per unit of volume -- areas of 1000 m^2/gm are not uncommon. The bulk of the area is on the walls of pores in the granule. The driving force for adsorption is a function of concentration of the material to be adsorbed, active surface area available, type of adsorbate and, to a lesser degree, pH and temperature.

B Various theories have been proposed for the adsorption phenomenon but, in general, the process mechanisms are still largely unexplained. One empirical formula, the Freundlich adsorption isotherm, states that the quantity of material adsorbed per unit weight of adsorbent is proportional to the concentration of solute in equilibrium with the adsorbent. This equation can be written as follows:

$$\frac{X}{M} = kC^{1/n}$$

where X = units of material adsorbed
M = weight of adsorbent
C = equilibrium concentration of materials remaining unadsorbed in solution
k& n = constants which have different values for each solute and adsorbent. They are also temperature and pH dependent.

This formula does not take into account the fact that the adsorbent will reach a saturation point at which further increases in concentration will not increase the loading.

C Figure 3 shows isotherm data taken by adding different amounts of adsorbent to given quantities of wastewater and measuring residual chemical oxygen demands after equilibrium has been reached. In the case of granular carbons, this may take several weeks so the carbon is pulverized for the test. The lines can be extrapolated to the feed concentrations (C_o) to determine the adsorption capacity of the carbon for the organic material in a given wastewater.

D Some generalities relating to the type of materials adsorbable by carbon are:

1 Weak electrolytes are absorbed better than strong electrolytes.

2 The more ionic a material is, the more difficult it is to adsorb.

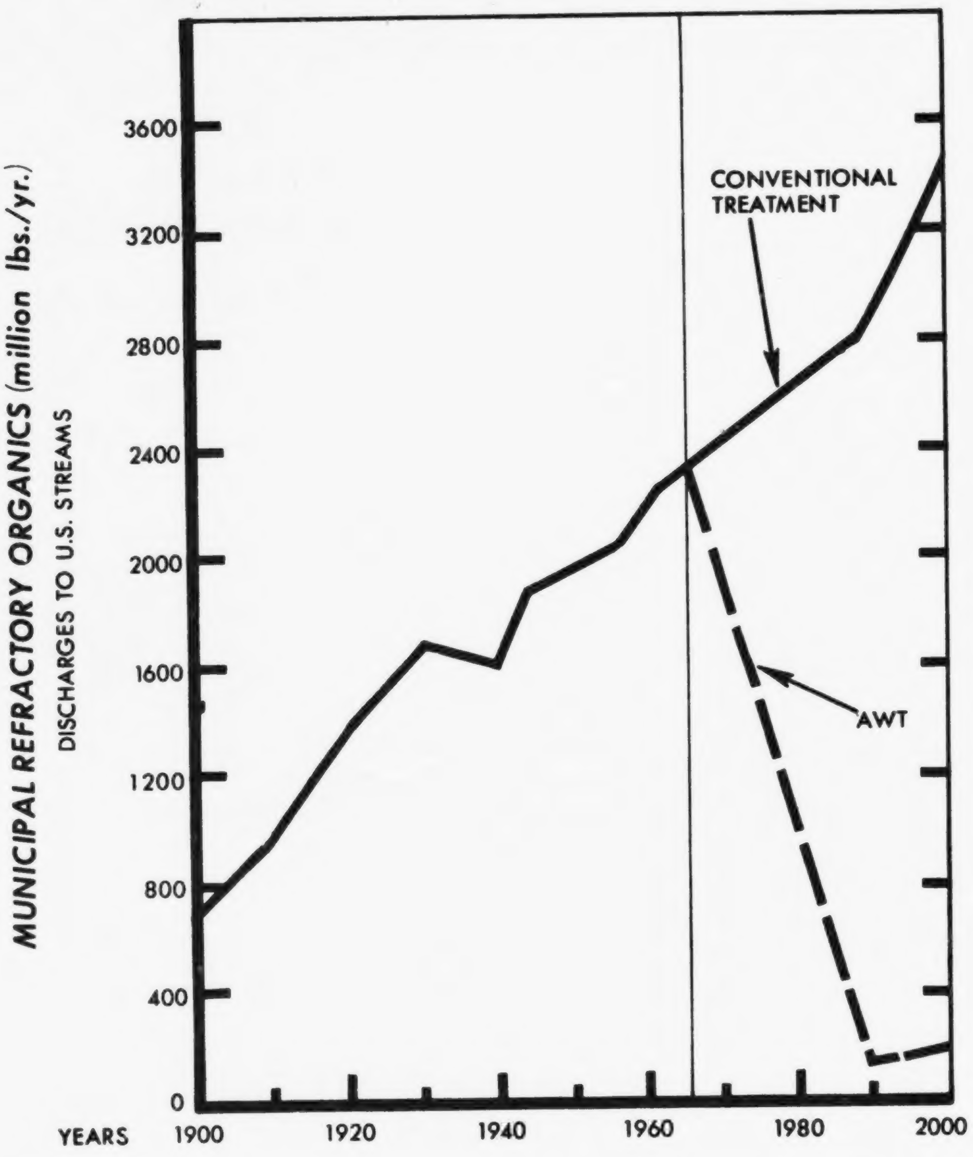
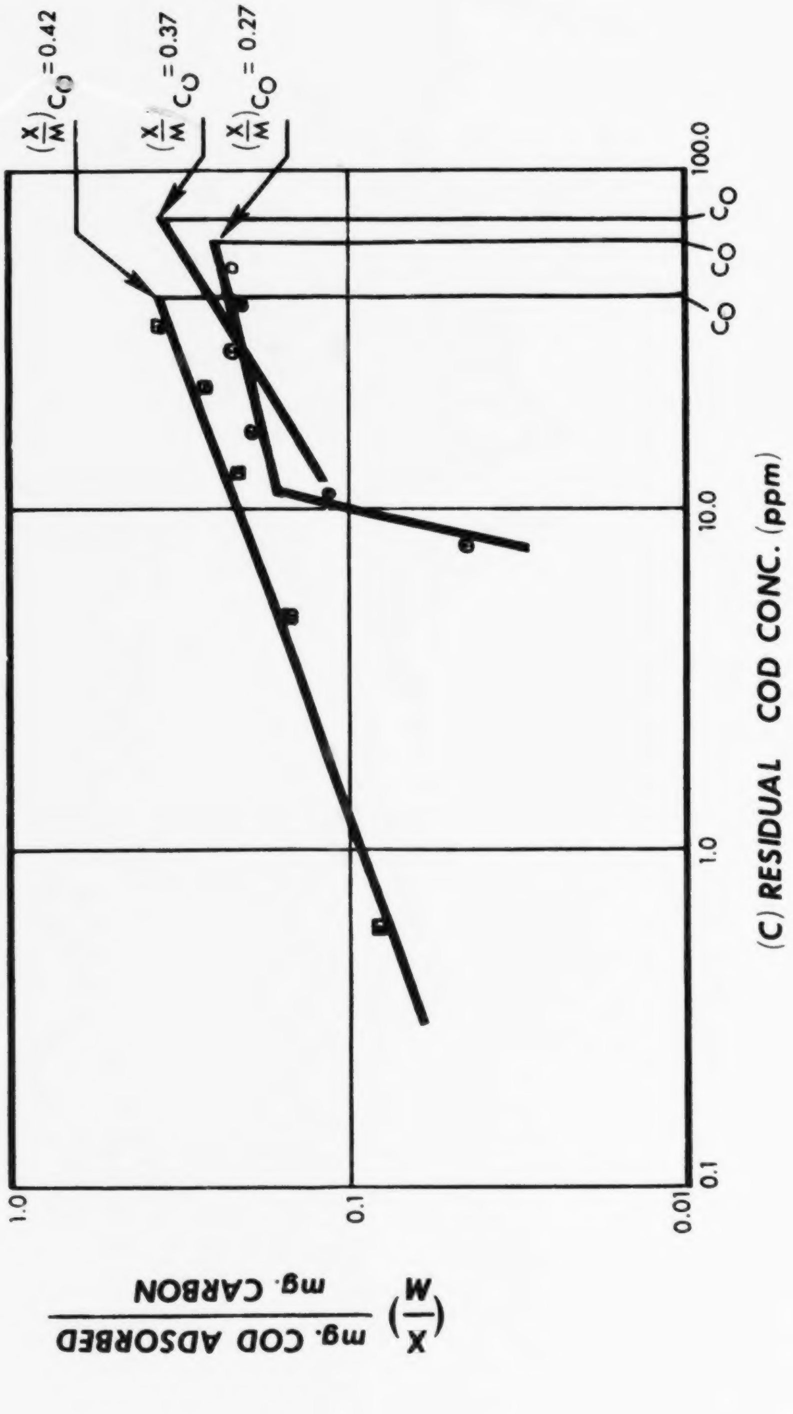


Figure 2. ESTIMATED LOAD OF MUNICIPAL REFRACTORY ORGANIC MATERIALS TO U. S. STREAMS

FIGURE 3: COD ISOTHERMS USING VIRGIN CARBON AND DIFFERENT SECONDARY SEWAGE EFFLUENTS



3 Sparingly soluble materials are generally adsorbed better than highly soluble materials.

4 High-molecular-weight materials may be adsorbed better than those of low molecular weight. There are exceptions: ABS, for instance, is a very soluble material and yet is absorbed well on carbon and other adsorbents.

In industrial and municipal waste, you have mixed materials that complicate the problem. When adsorption is applied to two materials such as phenol and ABS, each inhibits the other's adsorption. In general, however, the net effect of mixed materials is not detrimental, and you may get an enhancement of the total weight of materials adsorbed from mixtures.

IV LABORATORY STUDIES

A A detailed laboratory study of the performance of activated carbon as an adsorbent for organic materials was conducted by Drs. Morris and Weber of Harvard University under sponsorship of the Federal Water Pollution Control Administration.

B Figure 4, from this study, shows the effect of the molecular weight of the adsorbate molecule on the rate of adsorption. In addition to size, the molecular configuration has an effect -- extensive branching tends to reduce the rate of adsorption.

C As mentioned before, size reduction of the carbon reduces the time necessary for reaching equilibrium. Figure 5 shows the effect of particle size on adsorption rate. If the mechanism of adsorption is one of uptake on external sites, the rate should vary as the reciprocal of the first power of the diameter. If the mechanism is one of diffusion within the particle, the rate should vary with the reciprocal of the square root. This figure shows that intraparticle diffusion is the rate-controlling mechanism.

D Decreasing temperature and pH act to increase both the capacity of the carbon and the rate of adsorption. It seems evident at this time, however, that the cost of controlling either the temperature or pH far exceeds any benefit that could be obtained by this action.

E An effort was made to determine a relationship between the efficiency of a carbon for removing COD from wastewater and one or more of the classical methods for evaluating carbons. These classical methods include 1) surface area by nitrogen adsorption, 2) adsorption capacity for phenol and 3) adsorption capacity for methylene blue. None of these indices were useful in rating activated carbons for the service intended. The adsorption capacity for alkyl benzene sulfonate (ABS) came closest to being meaningful but still was not reliable enough to be used.

F At this time, our recommendation to a potential user would be an empirical test in which the waste to be purified is contacted with granular carbon in small-scale columns. Publication No. 8 in the selected reading list at the end of this outline presents a detailed procedure for arriving at a system design by this method.

V PILOT PLANT STUDIES AND RESULTS

A Carbon adsorption was tested by setting up small columns in series at a sewage plant in the Pittsburgh area. Figure 6 is a schematic drawing of the experimental apparatus.

B The principal conclusions drawn from these studies, from similar ones at a pilot plant area in Pomona, California (a joint project of the FWPCA and the Los Angeles County Sanitation Districts) and from others are as follows:

1 The COD in a well-treated secondary effluent can be reduced to less than 3 ppm by adsorption on carbon.

2 At feed rates between 4 and 10 gpm/ft^2, the product quality is a function only of column length. The actual velocity of the water past the carbon granule (in the range mentioned) has no effect so diffusion of the solute molecule to the surface of the carbon granule is not controlling. Figure 7 illustrates this point.

3 Recent indications are that, in sugar decolorizing at rates much below 4 gpm/ft^2, diffusion in the liquid becomes controlling. This is an extremely important point and is being checked out on wastewater.

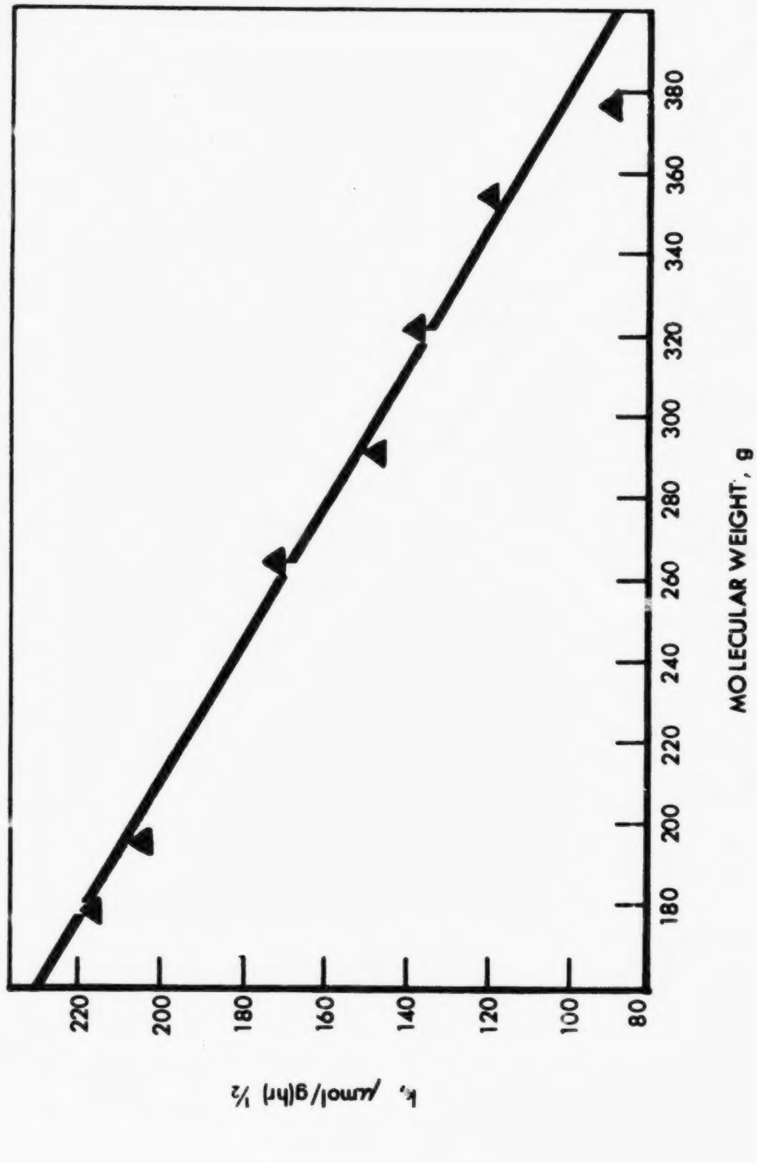


Figure 4. EFFECT OF MOLECULAR WEIGHT ON RATE OF ADSORPTION

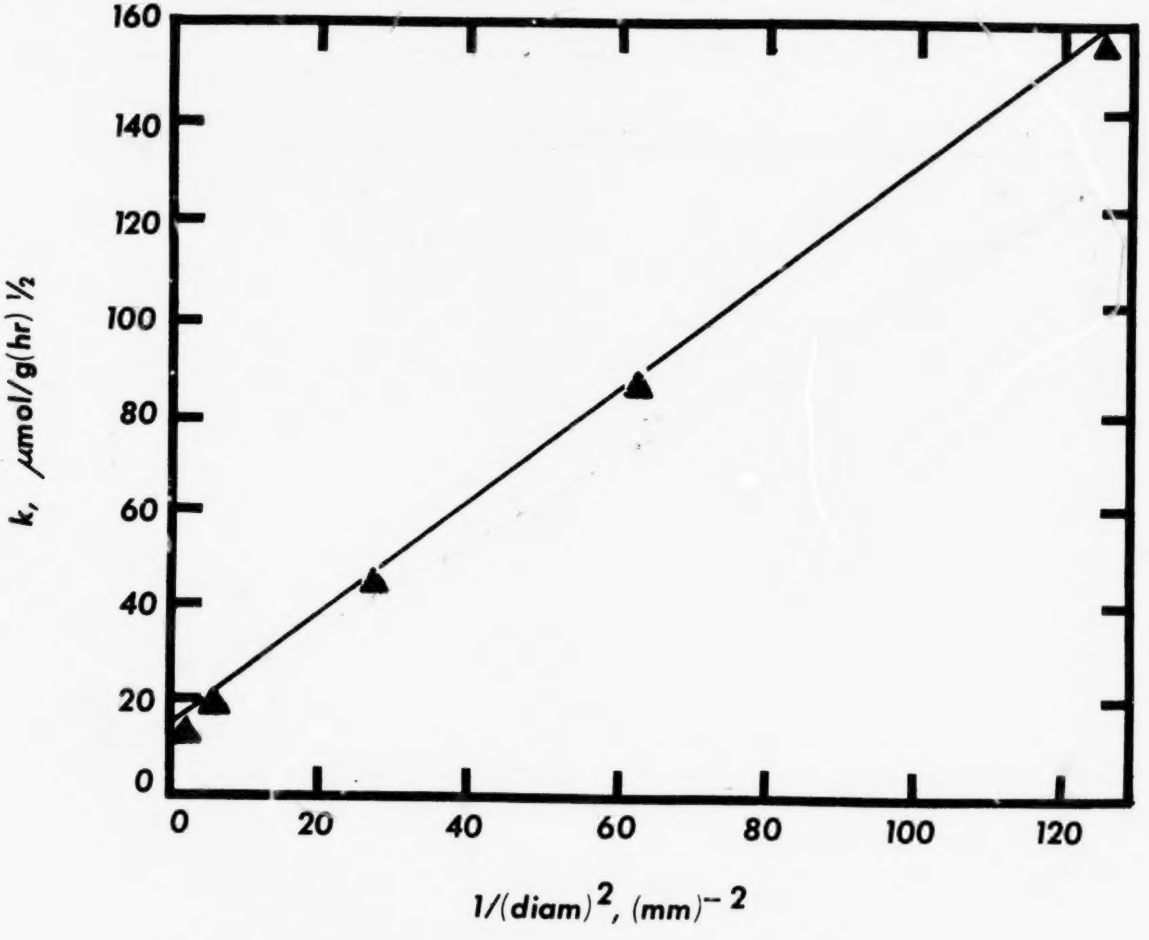


Figure 5. EFFECT OF PARTICLE SIZE ON RATE OF ADSORPTION

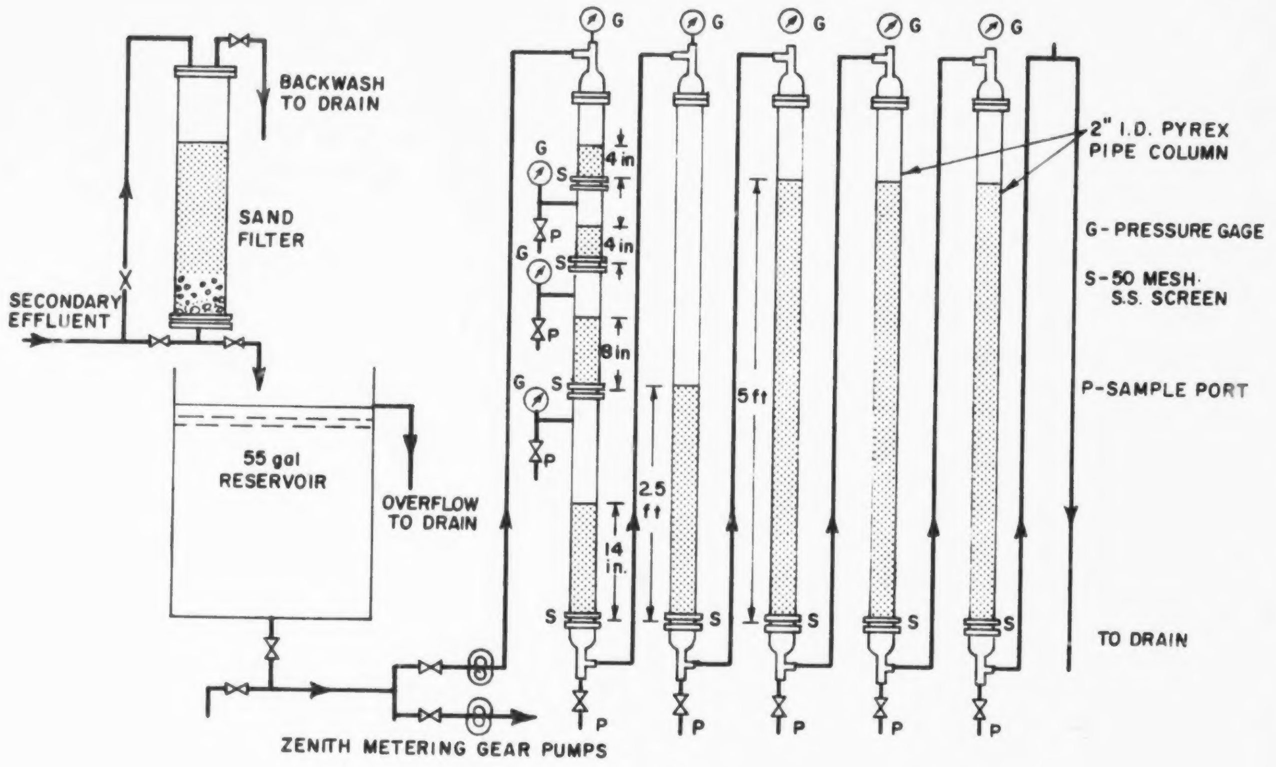
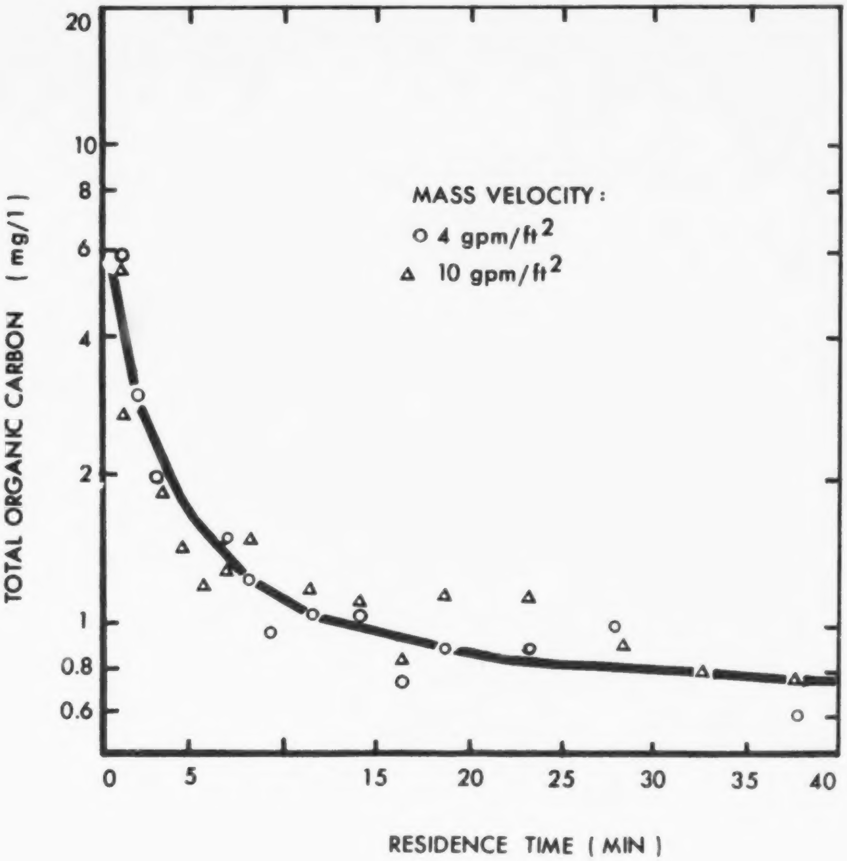

BACKWASH TO DRAIN
SAND FILTER
SECONDARY EFFLUENT
55 gal RESERVOIR
OVERFLOW TO DRAIN
ZENITH METERING GEAR PUMPS
G
S
P
4 in
4 in
8 in
14 in.
2.5 ft
5 ft
2" I.D. PYREX PIPE COLUMN
G-PRESSURE GAGE
S-50 MESH S.S. SCREEN
P-SAMPLE PORT
TO DRAIN

Figure 6. Apparatus for granular carbon column tests on secondary effluent

Figure 7. Effect of Mass Velocity on Carbon Column Performance



4 Granular carbon can be regenerated chemically and reused but does suffer a significant loss in capacity with each regeneration.

5 Recent studies at Pomona indicate that the nitrate ion can be removed from a nitrified secondary effluent in a carbon column. This is accomplished biologically and requires the addition of a supplementary food source (e. g. - methanol). The denitrifying bacteria utilize the oxygen from the nitrate ion to metabolize the methanol. The same results have been obtained in a sand media. Figure 8 shows recent results from Pomona.

C A 200 gpm pilot plant for treating municipal secondary effluent was built and is being operated at Pomona. Figure 9 is a schematic of this pilot plant.

1 **Contactor** No. 1 is operated at 200 gpm (7 gpm/ft^2) and the effluent is discharged to waste. When only 25% of the dissolved COD is being removed, the carbon is removed from the contactor, regenerated and returned to service.

2 Contactor Nos. 2 through 5 are operated in series. When the dissolved COD from the last contactor in series reaches 12 ppm, the carbon in the first contactor

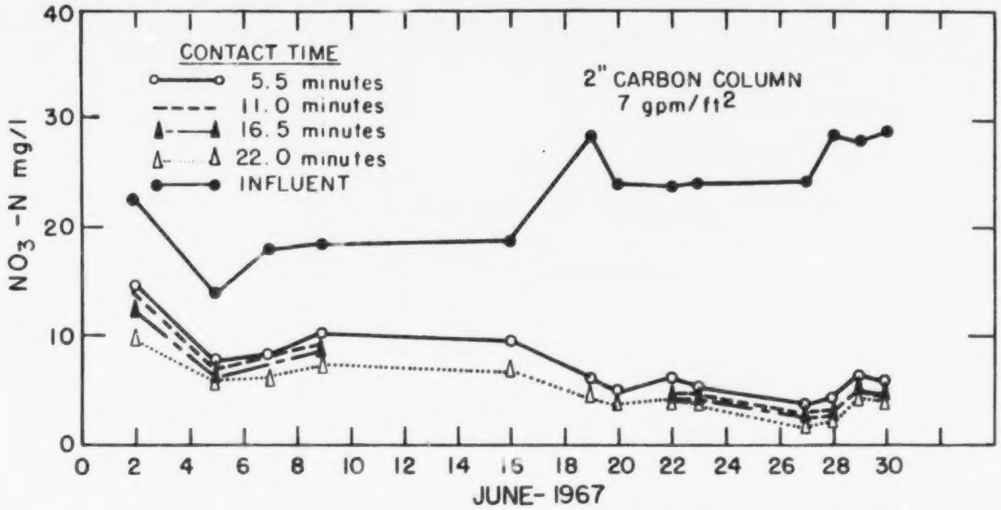


Figure 8. Denitrification on granular activated carbon

in series is removed, regenerated thermally and returned to the same contactor. The piping is then rearranged so that the contactor containing the freshly-regenerated carbon is last in the series . By this mode of operation, the carbon in the first contactor in series is nearly in equilibrium with the feed (and therefore contains the maximum possible loading of organics) and the freshest carbon contacts the water just before it leaves the system as product.

3 The performance of the four contactors in series over the first year of operation is shown in Table 2. After two years of operation, the carbon loading (in #COD/ 100 #carbon) is still about 58. The carbon dosage to maintain a maximum COD of 12 ppm is now about 350-400 #/mg.

4 Table 3 gives data on the quality of the feed and product over the first year. There has been no significant change over the second years operation. About 80% of the dissolved COD has been removed from the secondary effluent.

5 As of September 1967, the carbon in each of the four contactors in series had been regenerated twice. The carbon in the accelerated contactor, however, has been regenerated eight times.

6 A column of carbon never becomes completely exhausted. Dissolved COD removal levels off at about 15% -- this is evidently a result of biological activity on the carbon.

7 Very few BOD analyses have been run at Pomona. The BOD in both the influent and effluent are only about 5 ppm, which is below the level of reliability of the test.

D A 2.5 mgd granular carbon adsorption pilot plant has been in operation at Lake Tahoe, California for over two years. To protect the water of Lake Tahoe from increasing domestic wastes, it will soon be necessary to export the wastewater out of the Lake Tahoe Basin and export quality requirements cannot be met by secondary treatment alone. A 7.5 mgd plant is being built to meet this need. Figure 10 shows the flow sheet used in this plant.

FIGURE 9
CARBON ADSORPTION PILOT PLANT SCHEMATIC FLOW DIAGRAM

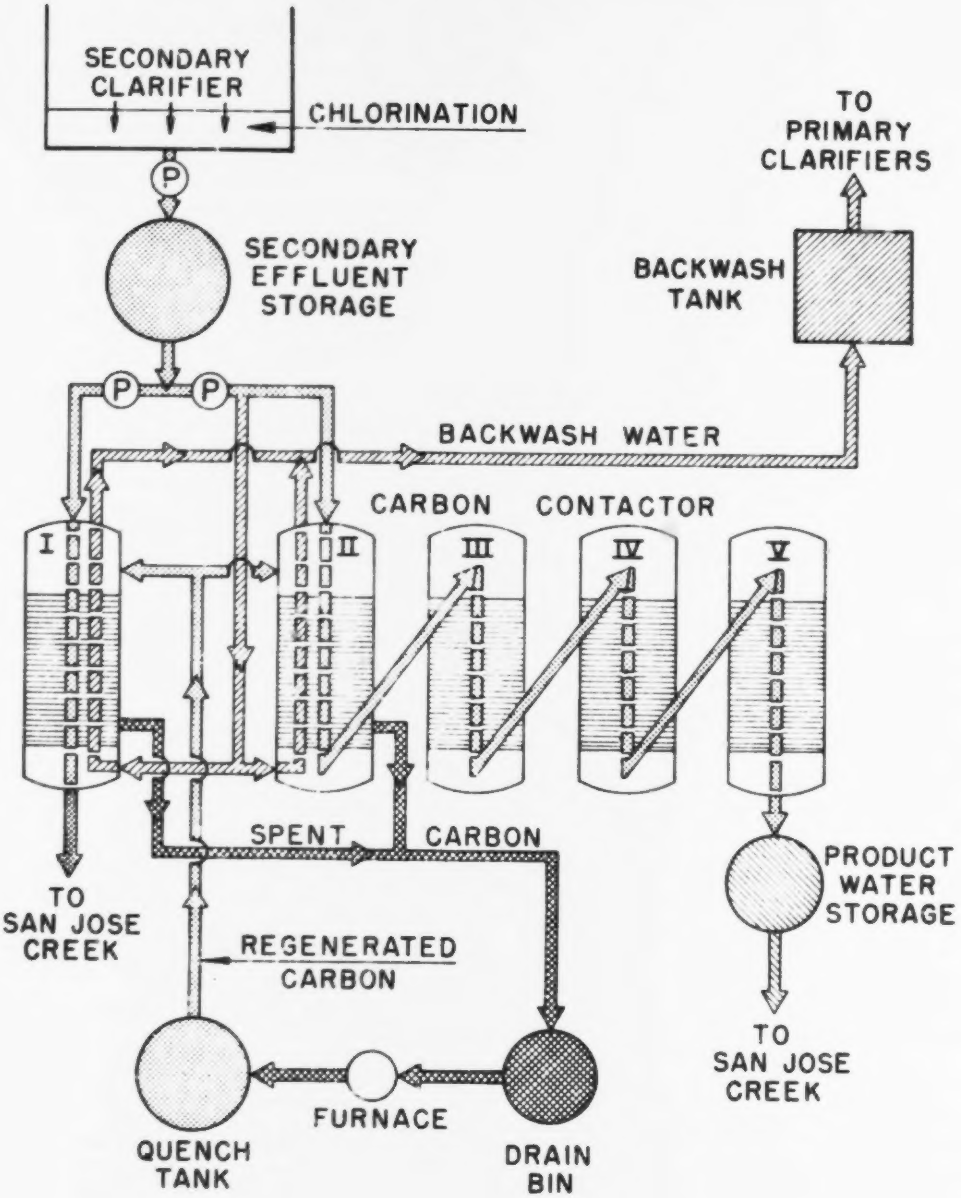

SECONDARY CLARIFIER
CHLORINATION
TO PRIMARY CLARIFIERS
P
SECONDARY EFFLUENT STORAGE
BACKWASH TANK
P
P
BACKWASH WATER
CARBON CONTACTOR
I
II
III
IV
V
SPENT CARBON
TO SAN JOSE CREEK
PRODUCT WATER STORAGE
REGENERATED CARBON
TO SAN JOSE CREEK
QUENCH TANK
FURNACE
DRAIN BIN

TABLE 2

MAIN CARBON COLUMN PERFORMANCE								
	I OA		II OA,B		III OA,B,C		IV OA,B,C,D	
VOLUME TREATED (MG)	24		59		81		100	
DAYS ON STREAM	86		211		288		365	
DAYS IN POS'N. "A"	86		125		77		77	
CARBON DOSAGE (lbs / MG)	280		220		250		270	
WT. OF ORGANICS REMOVED	T	D	T	D	T	D	T	D
COD lbs/100 lbs of carbon	73	46	122	66	106	57	87	58
TOC " " " " "	28	–	32	16	27	18	24	17
ABS " " " " "		5.3		5.1		4.9		2.8

T = TOTAL
D = DISSOLVED

TABLE 3

AVERAGE WATER QUALITY CHARACTERISTICS OF MAIN CARBON COLUMN

JUNE 1965 TO AUGUST 1966

PARAMETER		COLUMN INFLUENT	COLUMN EFFLUENT
SUSPENDED SOLIDS,	mg/l	10	<1
C O D,	mg/l	47	9.5
DISSOLVED C O D,	mg/l	31	7
T O C,	mg/l	13	2.5
NITRATE, as N,	mg/l	6.7	3.7
TURBIDITY,	J T U	10.3	1.6
COLOR,		30	3
ODOR,		12	1
C C E,	mg/l	—	0.014

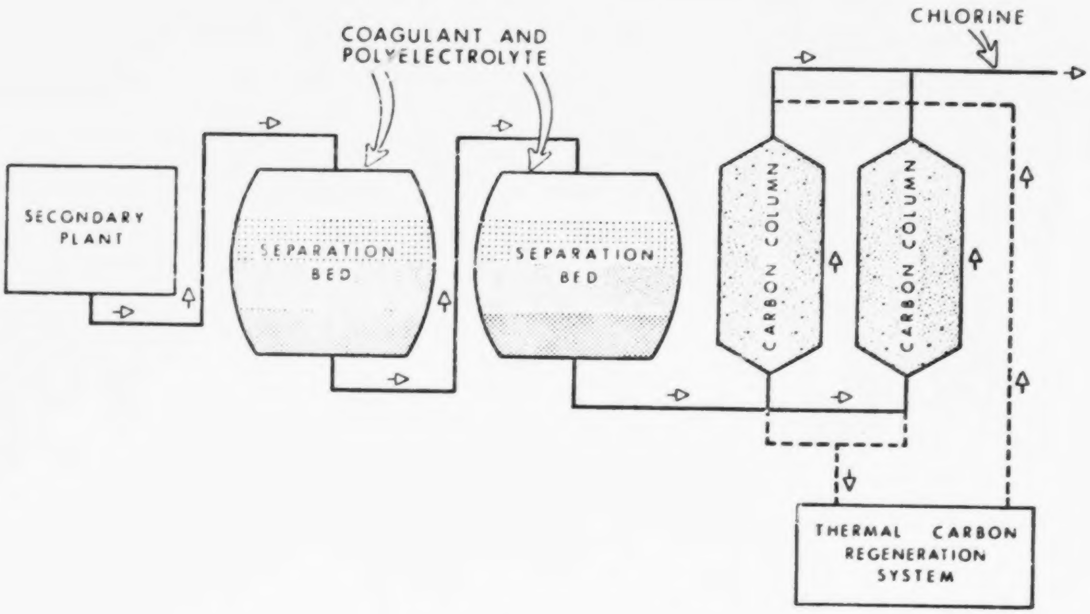

COAGULANT AND POLYELECTROLYTE
CHLORINE
SECONDARY PLANT
SEPARATION BED
SEPARATION BED
CARBON COLUMN
CARBON COLUMN
THERMAL CARBON REGENERATION SYSTEM

FIGURE 10 FLOW THROUGH ORIGINAL TERTIARY PLANT

1 Biological Oxygen Demand (BOD) is reduced from 200-400 ppm in raw sewage to <1 ppm in final effluent. COD is reduced from 400-600 ppm to 3-25 ppm. These data indicate that BOD is preferentially removed by carbon. A report recently issued by the South Tahoe Public Utility Districts claims 65% COD removal by the carbon columns.

2 Flow through the carbon columns at Tahoe is upward, in contrast to the down-flow at Pomona.

E A 30 gpm plant has been run at Nassau County, New York, to provide treatment to allow injection of treated wastewater. Secondary effluent was pre-treated by alum coagulation, sedimentation and filtration before carbon adsorption. A 400 gpm plant is presently under construction. The product water will be injected into the ground to prevent sea water intrusion and to replenish the groundwater supply.

VI REGENERATION

A Two types of regeneration have been studied - chemical and thermal.

1 Chemical regeneration, even by the strongest oxidants, was uneconomical. Hydrogen peroxide, the most effective regenerant tried, showed recoveries of 70% of the adsorption capacity on the first regeneration, 50% on the second and 20% on the third.

2 In the accelerated contactor at Pomona, the carbon has been regenerated eight times. Figure 11 shows the effect of these regenerations on the capacity of the carbon.

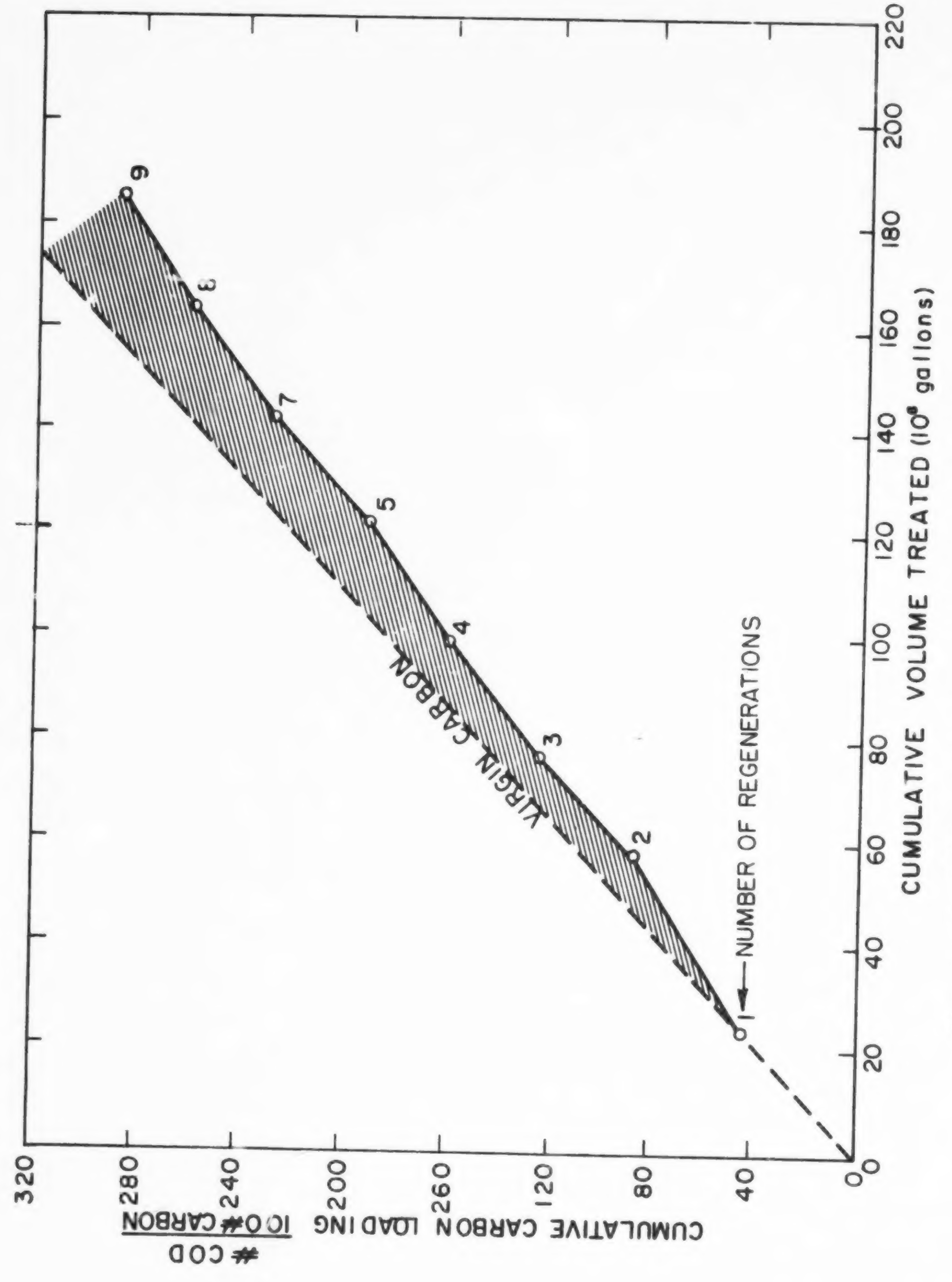


Figure 11. Effect of regeneration on carbon performance

B In a small plant in which installation of a regeneration facility could not be justified, the spent carbon can be burned as a fuel to produce power or heat. It may be economical to consider chemical regeneration (low capital cost) to prolong the life of the carbon.

C In a larger plant, a furnace can be used to obtain almost complete regeneration. All present installations use a multiple-hearth type furnace with rabble arms to move the carbon from hearth to hearth.

D Pollution of air from the furnace stack is a potential problem. At Pomona, we are investigating cyclone separators and afterburners. Lake Tahoe is using a water-scrubbing column on the stack gases.

VII COSTS

A Table 4 shows a breakdown of the total costs for a 10 mgd plant. Note that the amortization is for 15 years at 4%. This plant was designed to be identical in flow path and operating conditions to the Pomona Plant - that is, four pressure contactors in series, no pre-treatment, average product dissolved COD of 7 ppm. The capital cost is 16.7¢/gallon/day and the total cost is $83.00/mg.

B Lake Tahoe estimates that their 7.5 mgd plant can be operated for $30/mg. They predict 65% COD removal with a contact time about 1/3 of that in Pomona. In addition, Tahoe amortizes over 20 years at 4%. Similar amortization at Pomona would reduce the cost to $76/mg.

C Nassau County amortizes over 30 years at 3-1/2% and gets a cost of about $40/mg with a contact time of 24 minutes. Amortization over 30 years at 3-1/2% would reduce the Pomona costs to $67/mg.

D Figure 12 shows the estimated cost data for plants up to 100 mgd. These estimates may change as larger plants are built and more cost data are accumulated.

E The overall system needs to be optimized for costs. Some of the major factors that need to be considered are listed below.

1 Pressure vs gravity flow. Pressure tanks cost more but can be run at a higher rate and take up less area. Backwash requirements will be less for pressure systems. Gravity systems may require suspended solids removal before the carbon.

2 True countercurrent vs batch countercurrent. True countercurrent flow of carbon and water will utilize the maximum capacity of the carbon. We need to determine the cost of equipment for obtaining true countercurrent flows on a large scale.

3 Contact time. Contact time is inversely related to the rate at which the carbon is regenerated to maintain a given quality. Pomona could get the same quality product in three contactors if they regenerated at a higher rate.

VIII FUTURE PLANS

A In addition to the 7.5 mgd plant at Lake Tahoe and the 400 gpm plant at Nassau County, a 5 mgd plant is being planned at Piscataway, Maryland in the Washington, D.C. area; a 750,000 gpd plant in East Chicago, Indiana; and a 50,000 gpd plant in Santee, California.

B A contract has been initiated to study the effect on costs of types of contacting system used. Another study is in progress on the effect of carbon regeneration conditions on recovery of adsorptive capacity.

C Studies are in effect or being planned to determine the effects of carbon granule size, velocity of water past the carbon and type of carbon.

IX USE IN INDUSTRY

A Activated carbon is used in industry to improve the quality of wastewater but such use is not wide-spread. The main reason for this is that discharge standards do not yet require removals over and above those which can be obtained by conventional procedures such as settling, coagulation and biological treatment. It is clear that effluent quality standards will become more stringent and activated carbon is expected to find wide use in industrial waste treatment. Some of the present uses in industry are listed below.

1 Oil and phenolic compounds are removed from the effluent from a 20,000 barrel /day refinery in Bronte, Ontario at Trafalgar Refinery.

TABLE 4

COST ESTIMATE

FOR 10 MGD ACTIVATED CARBON TREATMENT PLANT

ITEM	COST/ MG
CAPITAL ($1,670,000; 15 YRS. @ 4%)	$ 41.00
POWER (1¢/KWH)	8.50
LABOR (4 MEN)	15.00
MAINTENANCE	5.00
CARBON REGENERATION:	
POWER, GAS & WATER	2.50
MAKEUP CARBON (10 % LOSS)	11.00
TOTAL	$ 83.00

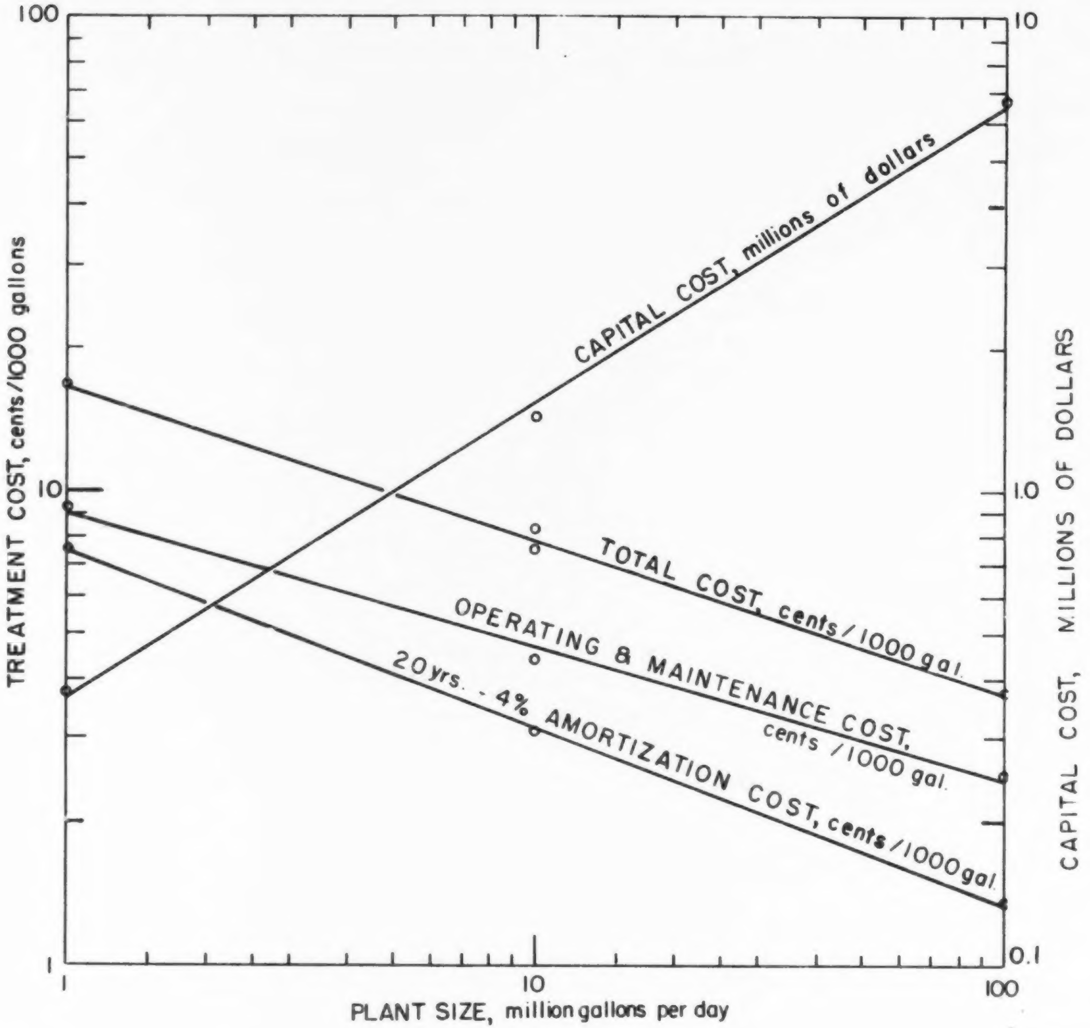


Figure 12 Cost estimates for granular carbon adsorption

Treatment level is about 5 ppm of carbon and phenol is reduced from 1.5 ppm to 15 ppb.

2 Caprolactam monomer is removed to beds of granular carbon in southeastern U. S. The monomer is recovered by a series of hot water extractions and the carbon is regenerated with steam. It is believed the process pays for itself through recovery of the monomer.

3 Dye wastes are being successfully treated using up to 265 ppm of powdered activated carbon. This dosage, followed by alum coagulation, removes 86% of the color.

4 The Wyandotte Chemical Company in Washington, New Jersey is removing mixed organic wastes from their effluent in a 20 ft. deep upflow column. They remove and regenerate 10-15% of the carbon every 14 hours. Most of their problems have been in transporting the carbon to and from regeneration. A carbon loss of 2% per cycle has been reported.

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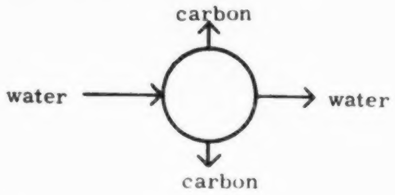
This outline was prepared by Arthur N. Masse, Chemical Engineer, Project Analysis Activities, Division of Research, Cincinnati Water Research Laboratory, FWPCA, SEC.

USE OF POWDERED CARBON IN WASTEWATER TREATMENT

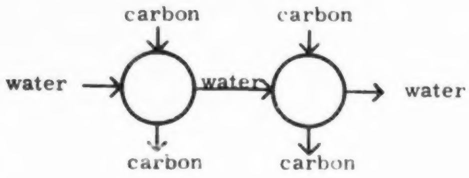
Powdered activated carbon is a highly adsorptive material and can be used to treat wastewater. Carbon can be produced with particle diameters of a few microns. The small particle size and the highly porous structure make it an ideal adsorbant. Powdered carbon has been used in the United States to remove taste and odor from water supplies since 1930. Currently, 40-45 million pounds of powdered carbon are used each year for water treatment. The successful use of powdered carbon has led to the investigation of its use for the treatment of wastewater.

I CONTACTING SYSTEMS

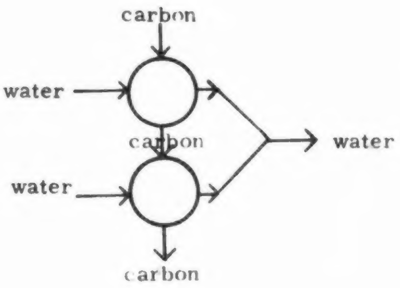
A Single Stage



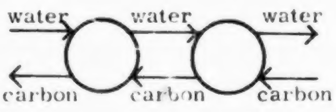
B Two-stage, Split Carbon Feed



C Two-stage Crossflow, Split Wastewater Feed



D Two-stage Countercurrent Flow



II PILOT PLANT STUDIES

Pilot plant studies have been made of the single stage and two-stage countercurrent flow systems.

A Single Stage - Tucson, Arizona

An Infilco Accelator unit[1] was used to investigate various aspects of wastewater renovation at the Tucson Municipal Sewage Treatment Plant (Figure 1). Beebe and Stevens reported water with a COD of 14-23.5 mg/l produced from a pretreated secondary effluent with a COD of 36-43 mg/l. Turbidity was reduced from 15-18.4 to values ranging from 1-6.9 units.

B Two-stage countercurrent flow - Lebanon, Ohio

Research has been conducted at the Lebanon, Ohio pilot plant facilities by the Federal Water Pollution Control Administration using a two-stage countercurrent flow system.

The pilot plant design (Figure 2) was based on contract work done by Dorr-Oliver[2]. Each stage consists of a contact tank, a flocculation tank and a settler.

The influent to the unit is pumped into a first stage contactor where it is mixed with partially spent powdered carbon from the second stage. The carbon water mixture overflows to the flocculation tank. During the passage from contact tank to flocculator, an organic polyelectrolyte is added to agglomerate the carbon and facilitate its settling. The floc is built up in the flocculation tank, from which the water overflows

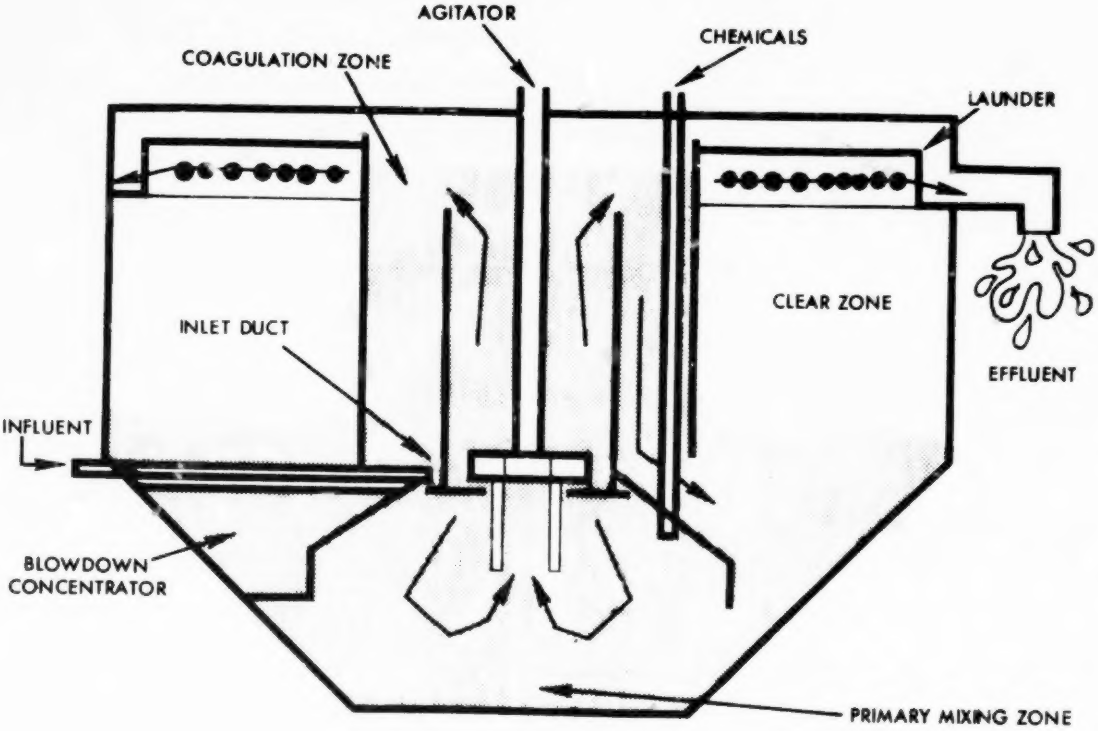


Figure 1. SINGLE STAGE TREATMENT UNIT

Reprinted with permission from January 1967 issue of "Water and Wastes Engineering."

to the settling tank. The carbon settled out at this stage has contacted the wastewater in both stages and will require regeneration for further use. The settler overflow is pumped into the second stage contact tank.

A virgin carbon slurry is added to the partially treated water in the second stage contact tank. The water carbon mixture again has a polyelectrolyte added, is flocculated and settled. The settled carbon is pumped to the first stage contact tank. The settler overflow is filtered through a dual-media filter (sand and anthracite). A tank is required to collect the filter backwash water so that carbon retained by the filters will not be lost from the system. The effluent obtained from this system is characterized by the data presented in Figures 3 and 4. Figure 3 shows that effluent turbidity is 1 or less Jackson Units until the influent to the system exceeds approximately 20 Jackson Units of turbidity. Figure 4 shows the relationship between the TOC of the influent and the TOC of the effluent. Assuming a linear relationship,

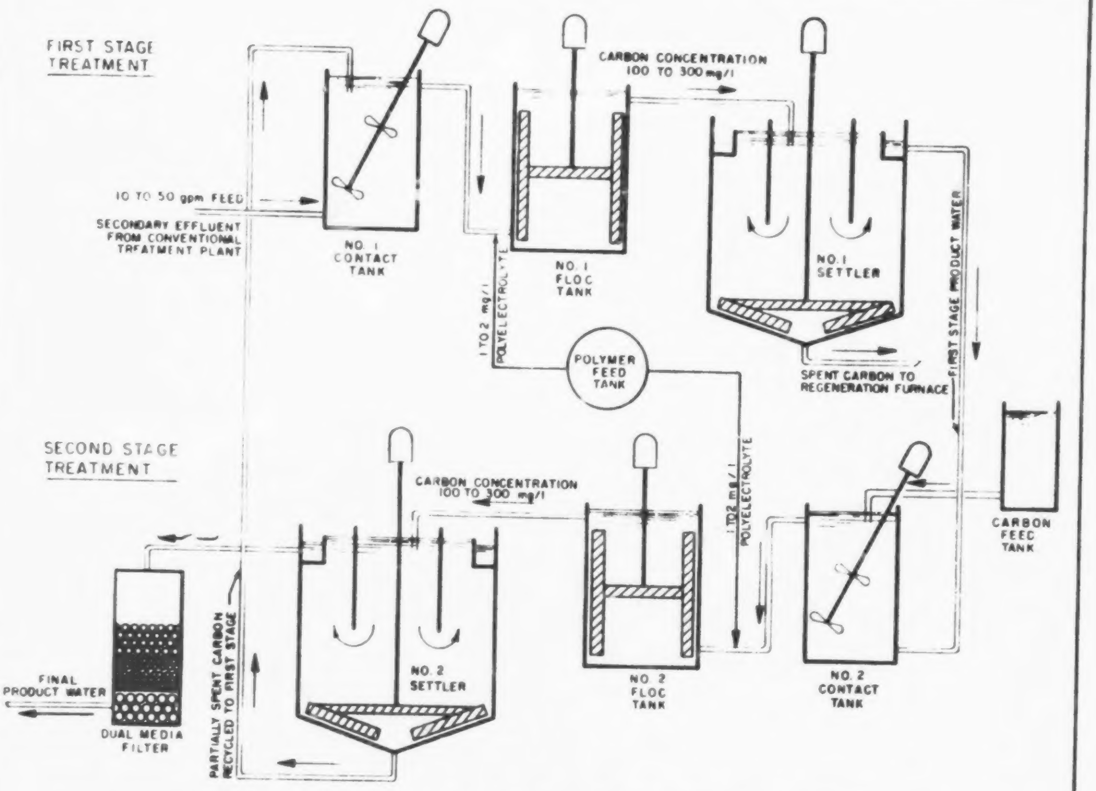

FIRST STAGE TREATMENT
10 TO 50 gpm FEED
SECONDARY EFFLUENT FROM CONVENTIONAL TREATMENT PLANT
NO. 1 CONTACT TANK
NO. 1 FLOC TANK
CARBON CONCENTRATION 100 TO 300 mg/l
NO. 1 SETTLER
1 TO 2 mg/l POLYELECTROLYTE
POLYMER FEED TANK
SPENT CARBON TO REGENERATION FURNACE
FIRST STAGE PRODUCT WATER
SECOND STAGE TREATMENT
CARBON CONCENTRATION 100 TO 300 mg/l
1 TO 2 mg/l POLYELECTROLYTE
CARBON FEED TANK
FINAL PRODUCT WATER
DUAL MEDIA FILTER
PARTIALLY SPENT CARBON RECYCLED TO FIRST STAGE
NO. 2 SETTLER
NO. 2 FLOC TANK
NO. 2 CONTACT TANK

Figure 2. POWDERED CARBON ADSORPTION PILOT PLANT
Lebanon, Ohio

the curve of best fit has the formula $Y = 1.23 + 0.06 X$, where Y = the TOC (mg/l) of the effluent and X = the TOC (mg/l) of the influent. This line appears to be representative until the TOC of the influent exceeds 25 mg/l, and shows a TOC reduction of over 90% of the TOC exceeding 1.2 mg/l. A TOC of 1.2 mg/l appears to be the lowest consistent value obtainable under the stated conditions.

These results were obtained using Lebanon secondary effluent and the given parameters. The parameters required to obtain a given effluent quality must be determined for each particular wastewater and situation.

Work has begun to determine the adaptability of this system for the treatment of primary effluent. The data obtained during two 120 hour runs is shown in Table 1.

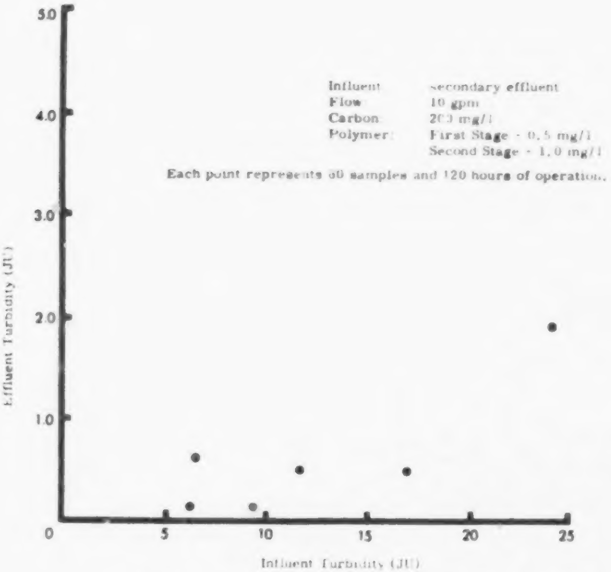


Figure 3. INFLUENT TURBIDITY VS. EFFLUENT TURBIDITY

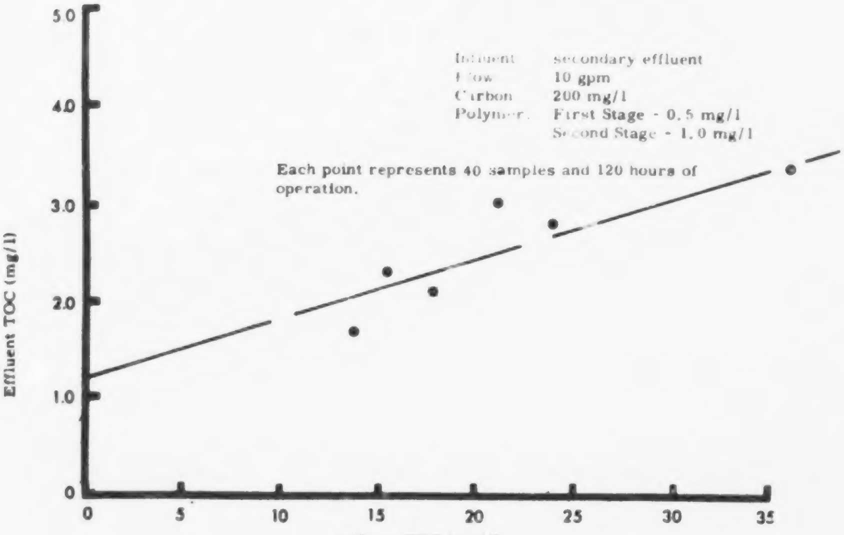


Figure 4. EFFLUENT TOC VS. INFLUENT TOC

TABLE 1

Influent: Primary Effluent
Flow: 5 gpm
Carbon: 200 mg/l(based on 5 gpm)
Polymer: 1st stage - 1.0 mg/l
2nd stage - 1.5 mg/l

June 13 - 17, 1967

TOC (ppm)	Feed	Product
High	216.0	32.5
Low	21.0	4.4
Avg.	69.0	10.2

Turbidity (JU)	Feed	Product
High	90.0	10.0
Low	12.5	0.83
Avg.	41.7	3.3

July 11 - 14, 1967

TOC (ppm)	Feed	Product
High	67.0	5.8
Low	14.6	1.6
Avg.	41.7	3.7

Turbidity (JU)	Feed	Product
High	38.0	2.8
Low	9.0	0.03
Avg.	23.4	1.0

III HANDLING POWDERED ACTIVATED CARBON (3)

Care must be used in the handling of powdered activated carbon. As with most finely pulverized material, there will be a dust problem if proper precautions are not taken. Dusting problems are minimized if the carbon is handled as a slurry whenever practical. Materials which come in contact with a carbon slurry should be corrosion resistant as activated carbon in water permits galvanic corrosion.

A Kraft Paper Bags

1 Until a few years ago, all powdered activated carbons were supplied in Kraft paper bags. The use of these bags involved transferring the bags to storage, moving the bags to the feed room, emptying the bags, and final disposal of the bags.

Storing the carbon in slurry form involves only emptying the bags and final disposal of the bags. This reduces the number of points at which dusting problems may arise.

2 The greatest amount of dusting occurs when the bags are emptied. The following precautions should be observed in order to minimize the dusting:

a The carbon bag should be opened only at the place it is to be emptied.

b The seam at the top of the bag should be removed by cutting it with a knife.

c The carbon should be allowed to flow out slowly during the emptying operation and never allowed to fall any appreciable distance. Cutting a hole in the opposite end of the bag will prevent a vacuum from developing within the bag and permit the carbon to discharge easily.

d The empty bags should not be shaken, since that will create dust without recovering a significant amount of carbon.

e The empty bags should be stored in a drum or barrel until such time as they are incinerated.

B Bulk Handling

Treatment facilities of a million gallons per day or larger should investigate the economics of bulk shipments.

1 Shipment

Powdered carbon can be shipped by railroad hopper cars and by Airslide railroad cars and Airslide trailers. Airslide railroad cars and trailers are specifically designed for bulk transportation of powdered commodities.

2 Handling

Bulk deliveries can be dumped directly into underground tanks where the carbon is wetted with water and stored until needed. The concentration most widely utilized is one pound of carbon per gallon of slurry. Higher concentrations have resulted in difficulties. The addition of one pound of powdered carbon will expand the volume of the resulting slurry about 10%. Slurry tanks should therefore have a minimum usable space of 40,000 gallons for Airslide cars, and 30,000 gallons for C&O hopper cars and bulk trucks.

Activated carbon is insoluble, and has a specific gravity greater than 1, therefore, agitation must be provided in storage tanks to maintain a uniform slurry.

C Transfer Pumps

Both Moyno and Duriron pumps have been used to transfer carbon slurries successfully. Other makes of pumps would also be satisfactory. Parts of the pumps that are in contact with the slurry should be corrosion resistant. A pump that incorporates ball check values could be troublesome at carbon concentrations of 10% or greater.

D Metering

Various metering pumps are suitable for feeding carbon. The literature[3] shows the Omega Rotodip feeder to be widely used in water treatment.

IV DESIGN

Only pilot plant facilities have used powdered carbon for wastewater treatment. The following information relates to pilot studies that have not been optimized.

A Single-stage Contactor - Infilco Accelator[1]

The pilot model accelator has a nominal flow rate of 5 gpm.
Tank: 5 feet in diameter, 3 feet deep
Liquid Depth: 35 inches
Liquid Volume: 400 gallons; 260 gallons of which are in the clarified liquid zone
Settler: Area = 17.2 sq. ft.
Rise rate = 0.29 gal/min/sq. ft. at 5 gals/min flow

Pressure Sand Filter: 42 inch diameter
Chemicals: Powdered carbon, ferric sulfate and polymer

B Two-stage Countercurrent Flow

The Federal Water Pollution Control Administration's pilot plant unit at Lebanon, Ohio, has a flow of 10 gpm.

1 Contact tank (2)

Dimensions: 26.75 in. diameter with a liquid depth of 31.5 in.
Volume: 75 gallons
Detention Time: 7.5 minutes

Mixer: 1750 rpm with two 3.3" diameter super-pitch propellers

Baffles: four 2" baffles attached to the wall

2 Flocculation tank (2)

Dimensions: 35 in. diameter with a liquid depth of 36 in.
Volume: 150 gallons
Detention time: 15 minutes
Mixing: gate-type flocculation paddle, 8 rpm

3 Settler (2) - gravity, conical bottom

Dimensions: tank - 53 in. diameter with a liquid depth of 49 in.
Volume: 515 gallons
Detention time: 51.5 minutes
Surface Area: 12.5 sq. ft.
Rise Rate: 1.25 gpm/sq. ft.
Bottom Scraper: 5 rph
Weir: peripheral, V-notch

4 Sand Filter: support - 1/4 in. to 3/4 in. stones
- 4 in. coarse sand

dual media - 9 in. of a 0.6 mm sand
-22 in. of Anthrafilt, effective size of 0.8 mm

V REGENERATION OF POWDERED CARBON

A To make the powdered carbon adsorption process economically attractive, a method for re-establishing the original adsorptive capacity to the spent powdered carbon must be developed. Davies and Kaplan[2] working with the Federal Water Pollution Control Administration conducted sufficient laboratory studies to indicate that a dewatered, spent powdered carbon can be regenerated to its original capacity with losses in the range of 1-5% by weight and an ash buildup of 2% by weight per regeneration cycle. Regeneration was carried out in a laboratory externally heated screw conveyor at a temperature of 750°F with a 20 minute detention time.

B It was recognized that serious heat transfer problems exist in this type of direct thermal regeneration and that a unit designed on this principle would be extremely large and would have great difficulty in reaching the required regeneration temperature. Accordingly, several methods are being studied to accomplish regeneration.

1 Microwave heating - Door-Oliver[4] (Figure 5)
Spent powdered carbon at about 10% solids will be dried in a rotary drum filter to about 30% solids. The filter cake shall then be dried in a Thermal Screw Dryer to approximately 75% solids. The dried cake will be processed in the Microwave Heating Unit.

2 Reaction furnace - FMC[5] (Figure 6)

Spent powdered carbon at about 10% solids will be pumped to a furnace. The carbon is rapidly heated to 1500-1600°F in the furnace by a burner which admits combustion products and excess air to pyrolyze and consume the pollution loading on the spent carbon. The steam regeneration carbon is then cooled to 150°F in a contactor such as a venturi scrubber.

3 Fluidized-bed - Battelle[6] (Figure 7)

The application of fluidization methods for regeneration of spent powdered carbon requires development of operating methods for proper fluidization of the fine powder. A fluidized bed of coarse, inert particles will be used as a constant-temperature zone. The spent, dried,

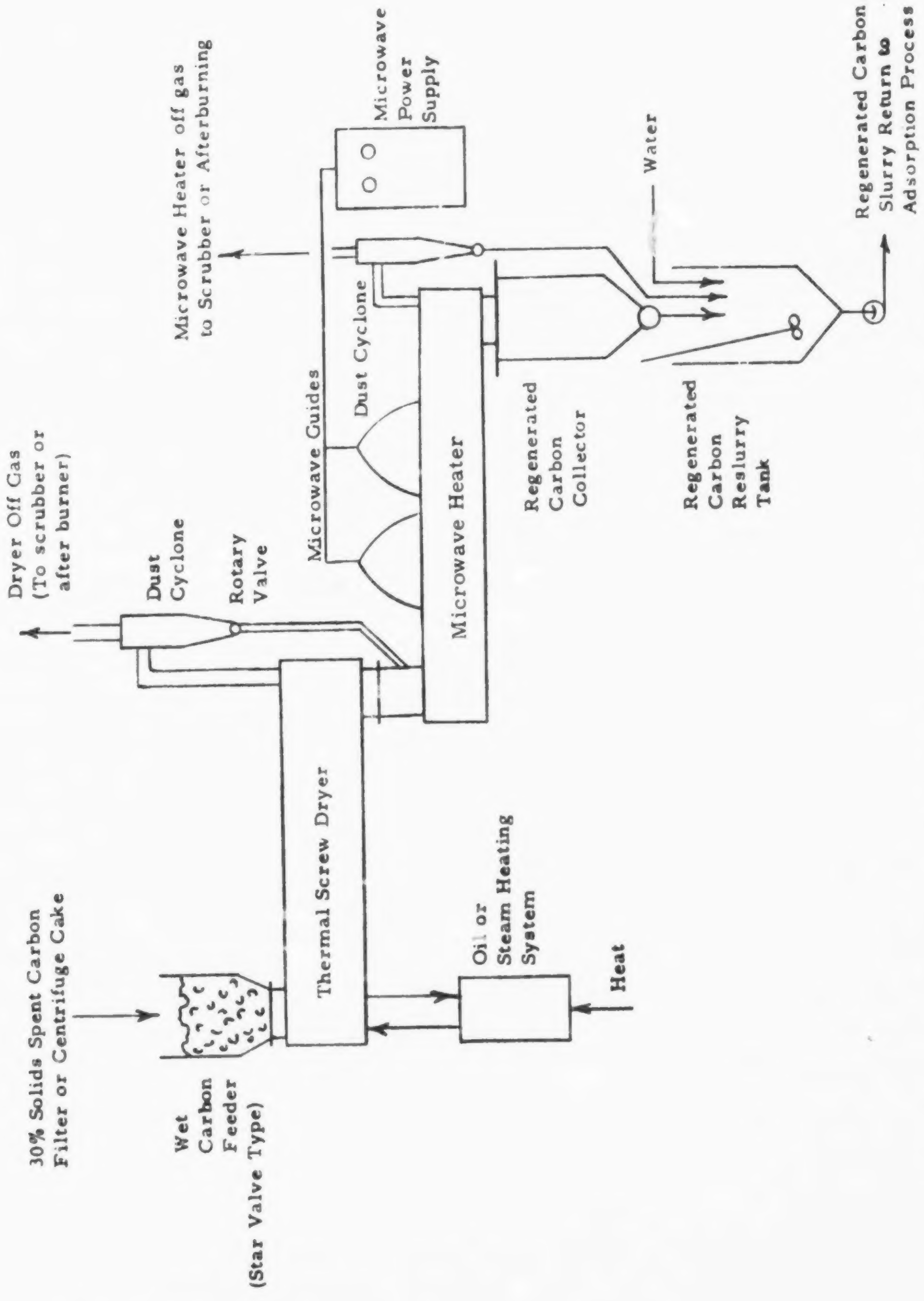
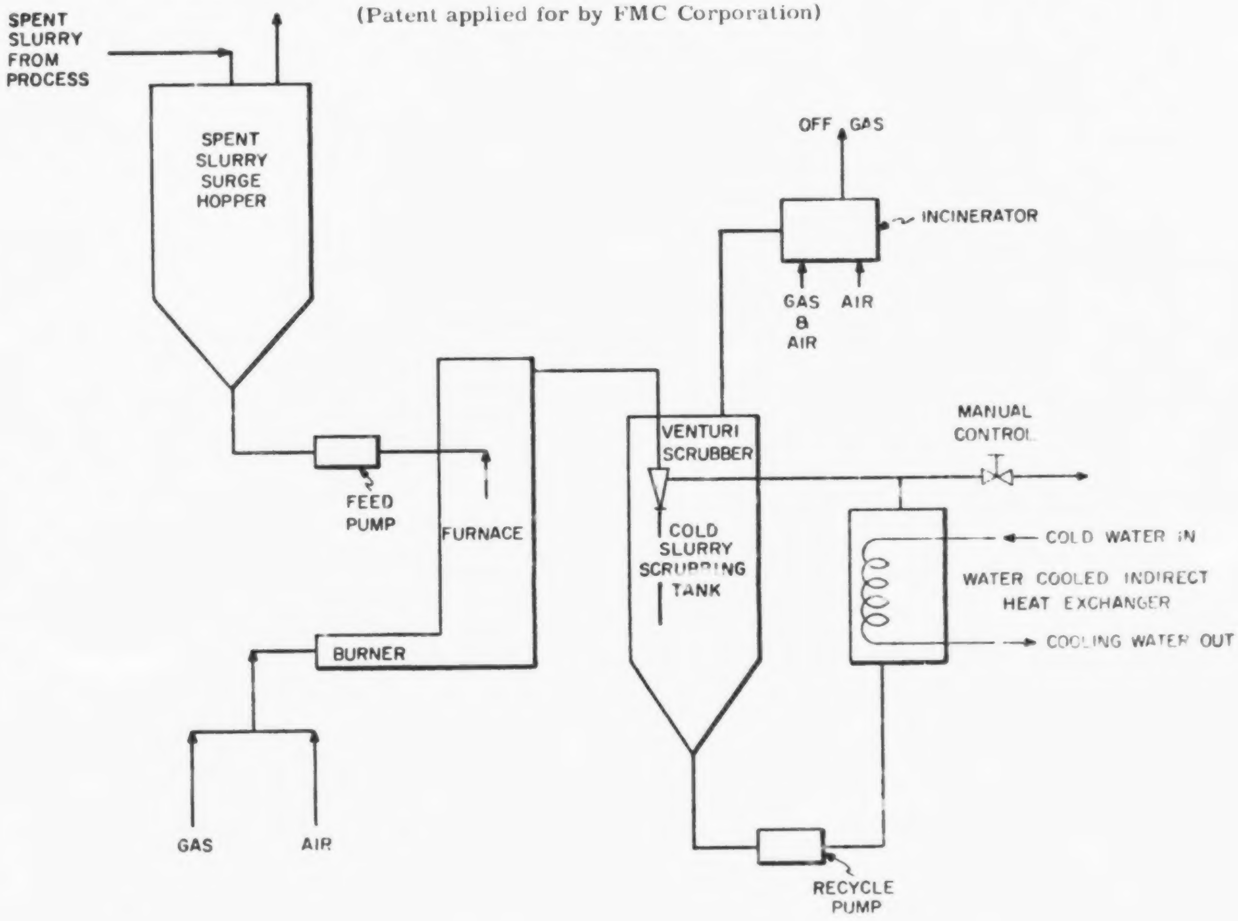

30% Solids Spent Carbon
Filter or Centrifuge Cake
Wet
Carbon
Feeder
(Star Valve Type)
Thermal Screw Dryer
Oil or
Steam Heating
System
Heat
Dryer Off Gas
(To scrubber or
after burner)
Dust
Cyclone
Rotary
Valve
Microwave Guides
Microwave Heater
Dust Cyclone
Microwave Heater off gas
to Scrubber or Afterburning
Microwave
Power
Supply
Regenerated
Carbon
Collector
Water
Regenerated
Carbon
Reslurry
Tank
Regenerated Carbon
Slurry Return to
Adsorption Process

Figure 5. Proposed Powdered Carbon Regeneration Process Utilizing Microwave Heating

Reproduced courtesy of Dorr-Oliver, Inc.

Figure 6. FLOW SHEET FOR PROPOSED BENCH SCALE AND PILOT PLANT

(Patent applied for by FMC Corporation)


SPENT SLURRY FROM PROCESS
SPENT SLURRY SURGE HOPPER
OFF GAS
INCINERATOR
GAS & AIR
AIR
MANUAL CONTROL
VENTURI SCRUBBER
FEED PUMP
FURNACE
COLD SLURRY SCRUBBING TANK
COLD WATER IN
WATER COOLED INDIRECT HEAT EXCHANGER
COOLING WATER OUT
BURNER
GAS
AIR
RECYCLE PUMP

powdered carbon would be fed into the bottom of the coarse, inert bed and carried through the inert bed by the action of the fluidizing gas. This method of fluidized-bed operation should offer control of retention time of the fine carbon powder and good heat-transfer characteristics. The finely divided carbon would be recovered with cyclone collectors or some other collection device.

C There are other methods of regeneration, Atomized Suspension Technique for example, but the above methods are those currently supported by the Federal Water Pollution Control Administration.

VI COST ESTIMATE FOR USE OF POWDERED CARBON

The cost estimates are based on work that has been completed and no effort has been made to optimize the design. The cost estimates are believed to be conservative.

A Some factors which would tend to reduce the estimated cost are given below:

1 Studies of regeneration that are in process. The estimated cost for

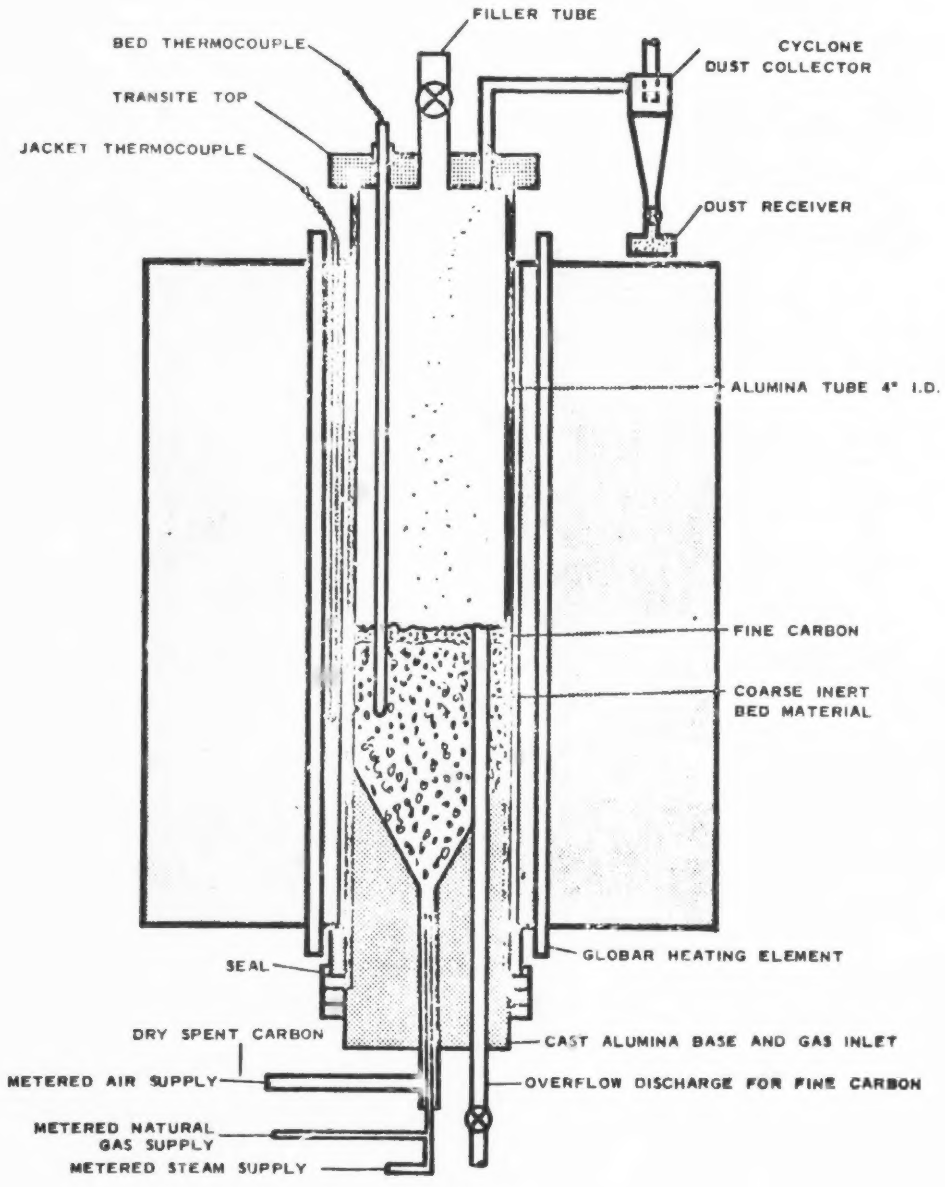

FILLER TUBE
BED THERMOCOUPLE
CYCLONE DUST COLLECTOR
TRANSITE TOP
JACKET THERMOCOUPLE
DUST RECEIVER
ALUMINA TUBE 4" I.D.
FINE CARBON
COARSE INERT BED MATERIAL
SEAL
GLOBAR HEATING ELEMENT
DRY SPENT CARBON
CAST ALUMINA BASE AND GAS INLET
METERED AIR SUPPLY
OVERFLOW DISCHARGE FOR FINE CARBON
METERED NATURAL GAS SUPPLY
METERED STEAM SUPPLY

FIGURE 7 EXPERIMENTAL FLUIDIZED-BED REGENERATION APPARATUS

Reproduced courtesy of Battelle Memorial Institute.

regeneration is based on a process (wet oxidation) that produces a powdered carbon that is not as active as some produced by other regeneration methods. The cost figure for carbon make-up can also be considered conservative because it is quite possible that there will be a smaller percentage of loss than the assumed 15%.

2 Contacting methods other than the method tested at Lebanon (a two-stage countercurrent process) are being considered. A contacting scheme utilizing a sludge-blanket type of settler or possibly pipeline contact may be effective. Improvements in the system could lower costs appreciably.

3 Research is underway to evaluate the properties of powdered carbons that would make them particularly suitable for treating wastewater. This would help to determine the best carbon for a particular waste and could result in a savings in material costs.

B Assumptions made in estimating the elements of cost are listed below:

1 A contact or rapid mix time of 7-1/2 minutes was assumed. The tanks were assumed to be 5 ft. deep.

2 The slurry mix tanks were assumed to be used to mix up a 10% slurry of carbon in water with a 2-hour mixing time. There were two stainless steel mixing tanks used.

3 Estimated use of powdered carbon 1.66 lb. per 1,000 gallons (200 mg/l in the feed stream).

4 Cost of powdered carbon delivered is 9¢ per pound. With no regeneration the cost of carbon alone is 15¢ per 1,000 gallons.

5 Virgin carbon slurry is 10% solids. Spent carbon slurry is 10% solids.

6 Cost of wet oxidation taken as 1.99¢, equivalent to about $24 per ton of dry solids.

7 A 15% overall loss or make-up require- is assumed.

8 It is assumed that the operating cost is equal to a conventional secondary treatment plant.
$\$/\text{mgd} = 5,000 + 21,500\ (1/\text{mgd})^{.63}$

9 The total detention time for the plant is 2-3/4 hours.

10 With 200 mg/l carbon feed, 1,910 lb. of carbon is in the 10 mgd plant.

11 Assumed overflow rate for settlers = 700 gal/day/sq. ft.

C The following list of cost elements is based on the preceding assumptions.

COST ANALYSIS FOR POWDERED CARBON ADSORPTION PROCESS

CAPITAL COST (10 mgd)

2 Settlers (700 gpd/sq. ft.)	360,000
2 Flocculators (15 min.)	94,400
2 Rapid Mix Tanks (2 hr.)	60,800
Filtration and Chlorination	450,000
Air Blowers (mixing)	16,000
3 Slurry Pumps	12,000
3 Main pumps	22,500
	$1,022,700

Multiply by 1.29 to correct for construction cost index = $1,319,283.

TOTAL COST POWDERED CARBON PROCESS

(cents/1,000 gallons)

	10 mgd
Amortization Cost (20 yr., at 4%)	2.6
Carbon Regeneration	2.0
Carbon Make-up	2.3
Operating and Maintenance	2.7
Organic Coagulant	1.3
Total Cost	10.9

VII POWDERED CARBON VS. GRANULAR CARBON

A Both processes have the capability to reduce organic contamination well below any other proven unit process. The processes, with regeneration included, do not create additional disposal or pollution problems.

B The powdered carbon process has further merit because:

1 It is readily adaptable to large scale treatment.

2 The quality of the effluent can be adjusted by changing the carbon concentration.

3 Regeneration can be incorporated into a continuous system.

4 The powdered carbon is handled in slurry form.

5 Pumps and facilities for handling the carbon have been proven in water treatment plants and in industry.

6 Powdered carbon has rapid adsorption rates.

7 There is a potential of treating primary effluent with powdered carbon.

8 A large carbon inventory is not required.

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This outline was prepared by Eugene F. Harris, Sanitary Engineer, Treatment and Control Research Activities, Cincinnati Water Research Laboratory, FWPCA, SEC.

CHEMICAL OXIDATION

I INTRODUCTION

Chemical oxidation has been used to a small extent in treatment of industrial wastewaters (1). Air oxidation has, for example, been applied to certain petroleum refining wastes for destruction of ammonia, hydrogen sulfide and mercaptans. Chlorine is sometimes used for destruction of cyanides and has been suggested along with ozone for destruction of phenols in coke manufacturing wastes. Generally, however, chemical oxidation has been found too expensive for industrial wastewater treatment. Although the process has not been applied on plant scale to municipal wastewater, cost estimates based partly on the results of laboratory studies with secondary effluent suggest a similar result (2) (3). The aim of work on secondary effluent was to remove the remaining organic contaminants. There are a number of oxidizing agents that are cheap enough to be practical if the amount of oxidizable materials is not excessive. The problem lies in applying the oxidizing agents in such a way that large excesses and long contact times can be avoided. The fact that there is a chance for oxidation to be practical makes it sufficiently interesting to consider further study.

II THEORY

Although there undoubtedly are inorganic materials in industrial wastes that might be affected by chemical oxidation, those materials to be considered here are the organics. The following discussion refers specifically to municipal secondary effluents, but should apply also to many industrial wastes. There are four groups of oxidants that can be considered for organic oxidation. These are active oxygen species such as ozone, hydrogen peroxide, and hydroxyl free radicals from other sources; elemental oxygen with or without a catalyst; chlorine and derivatives; and oxy acids or salts such as potassium permanganate. Electrochemical treatment can also be used, but this treatment is actually a method of producing oxidizing materials such as chlorine or active oxygen species in situ. It is not a cheap process for organic removal. Of the available oxidants those that have the most chance of being useful appear to be the active oxygen species and elemental oxygen. Chlorine may be useful also. The following discussion pertains primarily to the active oxygen forms.

The theory of oxidation in wastewater is not well known. It is complicated by lack of knowledge of the complete composition of the organic materials. One type of reaction that appears to be important is attack by free radicals, including chlorine and especially hydroxyl free radicals, on hydrogen atoms attached to a carbon atom. The hydroxyl radicals can be produced from chemicals such as hydrogen peroxide or by means such as ultraviolet or nuclear radiation. Reactions of the type $RH + \cdot OH \longrightarrow R^{\cdot} + H_2O$ can be postulated where R represents an organic molecule. The organic radical might combine with a hydroxyl radical forming an alcohol. The organic radical also might react in the presence of oxygen to form a peroxy radical, $R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$. The peroxy radical can react further with another organic molecule to give another free radical and a hydroperoxide,

$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

The production of a new free radical demonstrates autoxidation. If these radical producing reactions could be made to continue a large number of times, the result would be a very cheap oxidizing method.

Although these free radical reactions and others that can be written result in oxidation of the organic molecule, they do not explain a decrease in the concentration of organic carbon. To remove carbon from the water requires rupture of carbon-to-carbon bonds with formation of carbon dioxide. A number of types of compounds resulting from prior oxidative attack can undergo decarboxylation to carbon dioxide. Two compounds and their reactions are:

$$R\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CO_2H \rightarrow R\text{-}CH_2\text{-}CO\text{-}CH_3 + CO_2$$

$$HO_2C\text{-}CH_2\text{-}CO_2H \rightarrow CH_3\text{-}CO_2H + CO_2$$

These reactions and, no doubt, many others then result in a decrease of the organic content of wastewater.

III STUDIES WITH MUNICIPAL SECONDARY EFFLUENT

A Catalyzed Hydrogen Peroxide Oxidation

A laboratory study (2) was undertaken to determine the technical feasibility of combining hydroxyl free radical oxidation and molecular oxygen oxidation or autoxidation for destruction of the organics remaining in secondary effluent. Hydrogen peroxide at pH of 3 to 4 and in the presence of ferrous or ferric iron was used as a source of free radicals. Both forms of iron catalyst were found to give appreciable removal, of the organics in secondary effluent. Ferrous iron could be used at room temperature, but ferric iron required elevated temperatures. From 36 to 65 percent of the chemical oxygen demanding materials were oxidized to carbon dioxide and water. When the available oxygen from hydrogen peroxide was considerably less than the chemical oxygen demand of the water, some autoxidation was found to occur in the presence of pure oxygen. The degree of autoxidation was not sufficient to make the process practical. That free radicals are produced was demonstrated by carrying out a polymerization reaction that is free-radical initiated.

B Oxidation with Other Free Radical Sources

Although free-radical oxidation had been demonstrated, no cheap source of radicals was available to make the process practical. Two possible sources are corona electric discharge and nuclear radiation. A laboratory study of treatment by corona discharge gave very small removals of organics from synthetic and actual wastewater samples. Electric power requirements were impractically high. For destruction of the organics in secondary effluent power costs could be more than $1.00/1000 gal. A limited study of oxidation by nuclear radiation from a cobalt-60 source also indicated high costs. At 10¢/curie an optimistic estimate of treatment costs is 50¢/1000 gal.

IV PLANNED STUDIES OF MUNICIPAL WASTEWATER

Oxidizing agents that may be economical for secondary effluent treatment, if technical feasibility can be demonstrated, are atmospheric oxygen or pure oxygen, ozone, and chlorine. A study of catalytic oxidation with air is planned. Promising results from this work would be of great importance for organic removal. Investigation of ozone treatment of secondary effluent is also planned to determine the efficiency of oxidation. Preliminary work with chlorine in the presence of ultraviolet radiation indicates that the rate of oxidation of some organics is accelerated. Light catalyzed oxidation will, therefore, be explored further.

V APPLICATION TO INDUSTRIAL WASTES

Development of a catalyzed-oxygen oxidation process could be of great importance for industrial waste treatment. Atmospheric oxygen and even pure oxygen can be supplied cheaply enough that fairly concentrated wastes could be treated. Light catalyzed chlorine oxidation may have some applications, but these would be more limited. The inherently high cost of ozone limits its application to very dilute solutions. There may be, however, uses that have been overlooked.

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This outline was prepared by Dr. Carl A. Brunner, Chemical Engineer, Project Analysis Activities, Division of Research, Cincinnati Water Research Laboratory, FWPCA, SEC.

NEW DEVELOPMENTS IN SLUDGE HANDLING AND DISPOSAL

by

Robert B. Dean
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Fourth Technical Session
2:30 P.M.
Thursday, February 6, 1969

Symposium on Nutrient Removal and Advanced Waste Treatment
Portland, Oregon

13-i

NEW DEVELOPMENTS IN SLUDGE HANDLING AND DISPOSAL

I INTRODUCTION

A Pollutants removed from wastewaters must be treated in such a way that they will not pollute the environment.

1 A pollutant is a substance that interferes with the intended use of the environment.

2 Incineration to reduce volume of organic wastes must not lead to air pollution.

3 Likewise, the effluent from a scrubber used to control air pollution from a furnace must be treated to prevent water pollution.

4 Only three places to put polluting substances. Air, land, ocean. Not in surface waters.

5 Pollutant substances must be rendered innocuous either by dilution below background level or by locking up.

B Ocean Disposal

1 Barge to deep water and sink to bottom. Lock up on bottom.

2 Ocean pipeline to deep water and sink solids. Dilute and lock up. West Coast.

3 Ocean diffuser into well mixed area. Dilute, Gulf and East Coast Continental Shelf.

4 Food chains may concentrate poisons killing larger species.

5 Long pipelines contemplated to collect sludges to bring them to disposal areas.

C Land Disposal. Fill.

1 Not suitable for soluble substances such as salts.

2 Needs dewatering to produce solid that will bear a load. Useful for insoluble inorganic wastes.

3 Organics will putrefy and decay and may produce foul seepage and subsidence of the surface.

D Land Disposal. Surface.

1 Not suitable for solubles except nutrients in quantities utilized by plants.

2 Low cost dewatering; can handle liquid sludges.

3 Low cost oxidation of organic matter.

4 Most elements locked up on soil minerals.

5 Improves soil for agriculture and forestry.

6 Chicago planning long pipeline to carry sludge to waste lands.

7 Morgantown, West Virginia, planning to recover mine spoil with organic sludge.

E Disposal into Wells.

1 Wells into porous formations are unsuitable for sludges or liquids containing filterable solids.

2 Useful for salt disposal into saline aquifers.

3 May leak out and contaminate other waters.

4 Large volumes may produce earthquakes and land movement.

F Disposal into Underground Cavities

1 Natural salt domes in oil fields. Suitable for salts, acids, alkalis and sludges.

2 Limestone caverns. Danger of leakage if underground water is present.

3 Artificial caves, nuclear cavities. More suitable for radioactive wastes than sludges. High cost relative to other methods.

G Consider pollutants on an element-by-element basis. Fortunately do not have 101 problems as most elements will not be pollutants.

II ORGANIC SUBSTANCES

A Carbon, Hydrogen, Oxygen, Nitrogen, Phosphorus, Sulfur, Ash.

B Principal problem in disposal of organic sludges is water. Twenty to fifty times as much water as all other substances in waste.

C Carbon and hydrogen in organic compounds can be oxidized to CO_2 and H_2O which do not pollute the atmosphere. Avoid CO by proper furnace operation.

D Heat Production:

1 Oxidation of 1 lb. of organic sludges is sufficient to evaporate about 2 lb. of water. Up to 3 lb. for oily sludge since combined O as in carbohydrates reduces heating value.

2 Fuel value of sludge is determined by bomb calorimeter. Can be estimated from volatile solids content. Sludge is about half as good as coal on a dry weight basis.

3 High temperature oxidation uses all the heat of combustion to evaporate water left in the sludge and usually requires excess fuel.

4 Economics of incineration are therefore closely tied to dewatering by sedimentation, filtration, and drying.

E Treatment of wet sludge to aid further processing

1 Anaerobic digestion. Reduces solids about 50% by hydrolysis and fermentation to methane gas which is burned to CO_2 and water. Produces foul supernatant liquor which returns organics and nutrients to the plant for recycle.

2 Sludge cooking at 370° F. Improves filterability of solids. Returns 10-20% of the BOD and 60-80% of the nitrogen.

3 Wet oxidation - Zimpro at 350° F removes 15% of COD by oxidation; dissolves 25% of solids and 90% of nitrogen. Higher temperatures destroy more solids. Improves filtration, produces a foul supernatant liquor.

4 Aerobic digestion. Aerate for 1-30 days. Stabilizes solids, retains nutrients but does not aid dewatering.

F Oxidation and dewatering on land surfaces. An "old-fashioned" process.

1 Low cost dewatering if sludge can be sprayed on land.

2 Organics are oxidized by soil bacteria.

3 Nutrients and other pollutants are fixed to a significant extent and kept out of water supplies.

4 Soil is improved for agriculture or forestry. Low economic value as fertilizer but significant in some areas.

5 Must control putrefaction and spread of pathogens by pretreatment.

III. CHEMICAL SLUDGES

A. Lime

1. $CaCO_3$, $Ca_5OH(PO_4)_3$, $Mg(OH)_2$, $CaSO_4$, $Ca(OH)_2$Dewater in lagoon or vacuum filter.
2. Land fill
    - a. Alkaline due to excess $Ca(OH)_2$
    - b. Non-leachable $PO_4^{\equiv}$
    - c. $SO_4^{=}$ leaches out, 1300 mg/l
3. Recovery of CaO from $CaCO_3$ by burning.

B. Iron

1. $Fe(OH)_3$, $Fe^{+2} \cdot 2\ Fe^{+3}\ (OH)_8$, $FePO_4$, $CaCO_3$, $CaSO_4$ -- Dewatering more difficult.
2. Land fill.
3. Iron recovery rarely worthwhile.

C. Aluminum

1. $Al(OH)_3$, $Al\ PO_4$, $CaCO_3$.
2. Very difficult to dewater; Freezing.
3. Aluminate recovery may be practical.

IV. SPECIAL DEWATERING TECHNIQUES

A. Freezing -- Destroys colloidal structure; gives good filtration

1. Needs slow freezing over several hours after thawing.
2. Complete freezing and minimal mechanical agitation.
3. Most promise for Activated Sludge and Aluminum Hydroxide.
4. Does not increase strength of filtrate.
5. Does not kill organisms.

B. Radiation

1. Selectively attacks high polymers and may reduce water holding capacity.
2. Does not disinfect. May kill 90% of microorganisms.
3. Releases organics to filtrate.
4. Requires costly shielding.

C. Pressure Cooking -- 250° C (480° F)

1. Gives good filterability.
2. Strong "soup" needs further treatment.
3. Disinfects.

D. Cooking with SO_2 catalyst

1. Good filterability at lower temperatures and pressures.
2. Strong "soup" may have food value for livestock.
3. Disinfects.

E. Cooking with Oxygen -- Zimpro

1. High temperature to destroy organic solids (450° C)
2. Low temperature to get good filterability (250° C)
3. Produces "soup" that is difficult to treat.
4. Disinfects.
5. Power recovery not economical.

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DEMINERALIZATION OF WASTEWATERS

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Technical Seminar
Nutrient Removal and Advanced
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Portland, Oregon
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ELECTRODIALYSIS

I INTRODUCTION

Usually when water is used, there are added varying amounts of inorganic materials. In the case of domestic wastes, the increment amounts to about 300 to 400 mg/l. Most of the inorganic material is composed of ions common to natural waters. Also added are phosphate and nitrogen as ammonia or nitrate. Removal of the added material is obviously necessary to maintain the quality of the water. With industrial wastes, especially from industries dealing with metals, the inorganic materials added are heavy metal ions that may be very toxic. Their removal is even more important than the removal of the ions usually found in natural waters.

Electrodialysis is useful for the partial demineralization of fairly dilute waters. For practical application usually the total dissolved solids (TDS) concentration is about 2000 mg/l or less. Since municipal wastewaters nearly always have a TDS less than 1000 mg/l they are well within the range where the process should be economically feasible. Many industrial wastes also undoubtedly fall into the practical concentration range. With electrodialysis sufficient demineralization is usually carried out to reduce the TDS to 500 mg/l or slightly less. Further demineralization results in appreciable added cost.

II PRINCIPLES

A direct electric voltage impressed across a cell containing mineralized water will cause positively charged ions or cations to migrate to the negative electrode and negatively charged ions or anions to migrate to the positive electrode. If cation- and anion-permeable membranes are placed alternately between the electrodes as shown in Figure 1, alternate compartments become more concentrated while the intervening compartments become diluted. Many membranes can be placed between the electrodes forming many dilute and many concentrate compartments. Manifolds can then be added so that the membrane stack can be fed continuously and demineralized product and waste concentrate streams can be removed continuously.

The cation(+) and anion(-) permeable membranes that make electrodialysis possible are composed of ion exchange materials. Cation membranes are likely to be sulfonated styrene with divinylbenzene added for cross linking and strengthening of the polymer. Anion membranes are also often styrene base with various amine groups being used to give the ion exchange property. The sulfonate and amine groups make the membranes very hydrophilic. Membranes absorb appreciable water when in contact with aqueous solutions.

Although the structure and function of the membranes is complicated, a rough quantitative explanation of the reason for their ability to transport ions of one charge can be obtained from consideration of the Donnan principle. This principle, in an incompletely rigorous form, states that the ion concentration product of a compound will be equal for water in the membrane and for the surrounding solution. A cation membrane in contact with very dilute sodium chloride can be considered as an example. The product of the concentrations of the sodium and chloride ions will be very small in dilute solution. In the structure of the membrane there will be a high concentration of fixed negative charges which, to maintain electroneutrality, will attract an equal number of positive charges or in this case sodium ions. The concentration of sodium ions associated with the water in the membrane will then be very high in relation to the original solution concentration. By the Donnan principle the chloride ion concentration in the membrane must be very small. If a voltage is applied across the membrane, sodium and chloride ions will move in opposite directions through the membrane. Because of the preponderance of sodium ions, however, most of the current will be carried by that ion. The cation

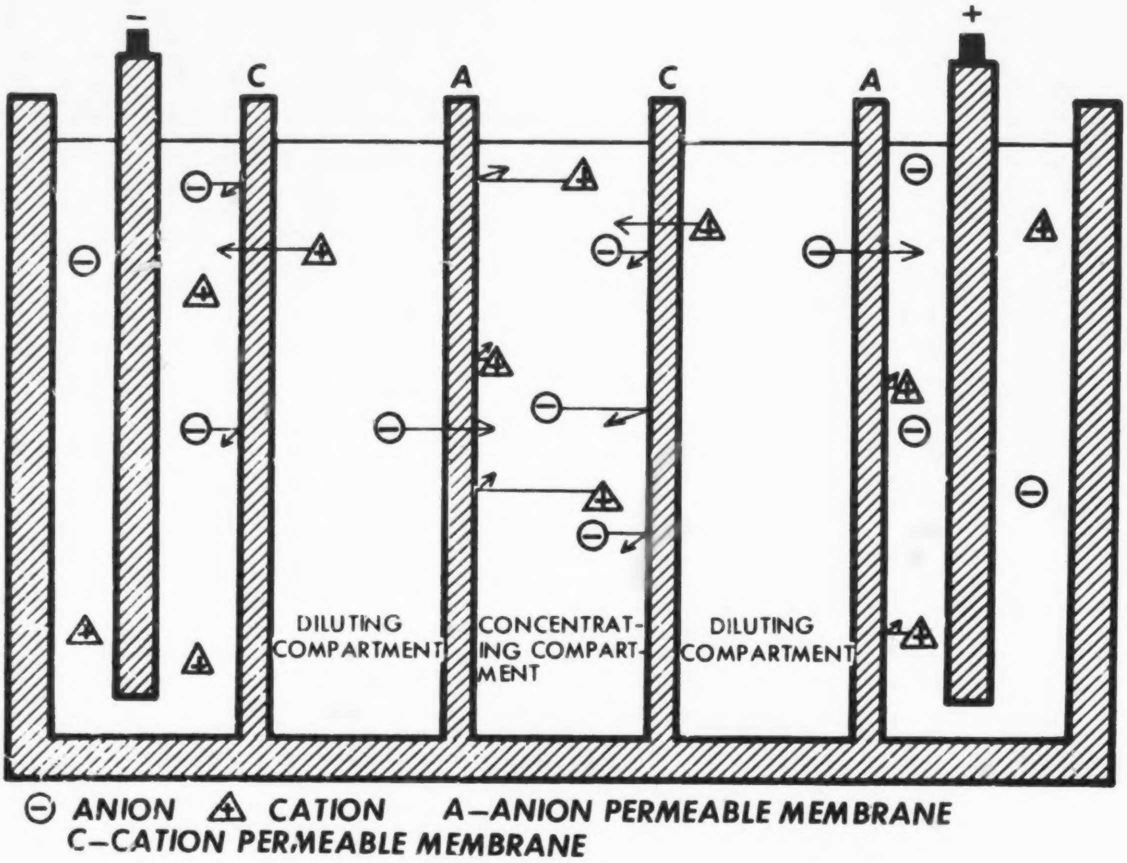
−
+
C
A
C
A
DILUTING COMPARTMENT
CONCENTRATING COMPARTMENT
DILUTING COMPARTMENT
⊖ ANION ⚠ CATION A–ANION PERMEABLE MEMBRANE
C–CATION PERMEABLE MEMBRANE

Figure 1. Electrodialysis Principle

membrane will, therefore, have a high selectivity for sodium and for cations in general. A similar argument can be used to show why anion membranes are selective to anions. As the Donnan principle indicates, selectivity decreases as solution concentration increases.

One of the important factors to be considered in operating an electrodialysis stack is the electrical power requirements. In treatment of wastewater, fortunately, this is not as important as in demineralization of a more highly mineralized water. Since direct current is used for electrodialysis, the stack power is simply the product of the current and voltage. The demineralizing current can be calculated from the product of feed rate per diluting compartment, concentration change from feed to product water expressed as normality, and Faraday's constant, 96,500 coulombs/equivalent. The required voltage is more difficult to determine. Classical thermodynamics allows the minimum voltage to be calculated (1) for a membrane separating solutions of different concentrations. In the usual electrodialysis application this minimum voltage, which only applies strictly at a zero current, is a small fraction of the total. The usual approach is to consider the stack as a series of resistances for which the voltage can be calculated from Ohm's law. Resistances that should be included are diluting and concentrating liquid streams, membranes, and the thin stagnant liquid films adjacent to the membranes. Usually, however, the resistances other than those of liquid streams are simply combined as a single value which must be determined experimentally. This empirical resistance can then be used to estimate the approximate voltage for an electrodialysis stack using the same kind of membranes. To calculate the total power requirements the voltage requirements of the electrodes and electrode compartment streams must be added to the voltage for the remainder of the stack.

III OPERATING PROBLEMS

The stagnant liquid films that occur at the membranes are responsible for significant problems during operation. Serious concentration gradients can develop across these films because of the higher electrical transference numbers in the membranes compared to transference numbers in solution. As a result there is a decrease in concentration from bulk dilute stream to the membrane surface and an increase in concentration from bulk concentrate stream to the membrane surface. The high concentration at the face of the membranes on the concentrating side leads to scaling from precipitation of compounds with low solubility. The low mineral ion concentration at the dilute side of the membranes causes transfer of hydrogen and hydroxyl ions from the water through the membranes. Polarization is the term used to describe operation when water decomposition becomes significant. The decomposition of water into ions wastes electric power. A more important effect, however, is the increased scaling potential at the concentrate side of the anion membranes. Hydroxyl ion increases the precipitation of magnesium hydroxide and calcium carbonate.

An effect that is common to electrodialysis is membrane fouling. This phenomenon is different from scaling since it involves deposition of materials on the dilute side of the membranes. Although there can be a number of causes in wastewater treatment fouling appears to be due to electrophoretic movement of negatively charged colloidal particles to the anion membranes. Because of the size of the particles they cannot move through the membrane. Instead they form a layer at the membrane surface that interferes with demineralization.

IV APPLICATION TO MUNICIPAL WASTEWATERS

A Laboratory Investigation

Bench scale study (2) of electrodialysis for treatment of municipal secondary effluent indicated that good removal of soluble and insoluble organic materials was necessary for satisfactory operation. Cellulose cartridge filters were used for removal of the suspended organic solids. These filters, however, would not be practical on a large scale and would have to be replaced by another form of suspended solids removal. Granular activated carbon was used for soluble organic removal. Using adequate pretreatment the cost of electrodialysis, exclusive of pretreatment and waste concentrate disposal, was estimated at less than 10 cents/1000 gal.

B Pilot Plant Investigation

As a result of encouraging results from the laboratory study a pilot scale investigation was undertaken (3). Equipment was installed at the Lebanon, Ohio Sewage Treatment Plant. Secondary effluent was the feed to the system. Based upon the experience gained from the laboratory work, clarification and soluble organic

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removal were considered necessary pretreatment for the electrodialysis stack feed. Diatomaceous earth filtration, using for the most part an alum treated water grade filter aid, was chosen as the method of clarification and granular carbon in fixed beds was chosen for adsorption of soluble organics. The pilot system is shown in Figure 2. The electrodialysis stack is an Ionics Mark III capable of holding up to 150 cell pairs. It is designed to remove about 40 percent of the TDS from the feed. Membranes for this stack are 18 × 40 in. and have about 3000 m^2 active area. Spacer material and edge gasket are combined in one piece. Spacer thickness is 0.032 in. Using all 150 pairs the nominal capacity of the stack is 50 gpm product water. As a result of difficulties with the diatomaceous earth filter, it was necessary to reduce the feed water rate. The number of cell pairs was reduced to 125 and the product rate to 42 gpm. The concentrate waste rate at reduced feed rate has been 4 gpm. Internal recirculation of concentrate at a rate about equal to the product rate is necessary, however, to maintain approximately equal pressures on both sides of the membranes. The pH of the concentrate stream is held at 5 or less to prevent calcium carbonate scale formation.

Operation of the pilot plant has resulted in only one serious problem, fouling of anion membranes. Membrane fouling increases stack resistance and necessitates higher voltage to maintain the desired degree of demineralization. Figure 3 shows how demineralization at constant voltage was affected by fouling. Fouling rate depends to some extent upon feed turbidity as might be expected. The unexpectedly low fouling rate for the run made after the stack was acid rinsed at a low enough pH to kill organisms suggests biological growth on the membranes as a contributing factor. Fortunately fouling has not been permanent. Shutdown over a weekend has always restored the fraction demineralization to near normal. Even with some fouling, operation is considered practical since excess stack capacity can be provided to take care of down time for self-cleaning of membranes. Control of feed turbidity is necessary for practical run lengths before shutdown is required.

Scaling of anion membranes, a problem that is serious in many electrodialysis installations, has not been particularly troublesome in treatment of municipal wastewater. Calcium carbonate scale formation has occurred on occasions, but has not done serious damage to membranes. Failure to control the pH to 5 or less can cause serious scaling that ruins the anion membranes. In the pilot work concentrate blowdown has been held at 9.5 percent of the product. Scaling potential would be reduced if the amount of blowdown were increased. Such an increase would, however, increase the problem of brine disposal. From a pollution control standpoint, therefore, the concentrated waste must be kept as low in volume as possible.

Permanent damage to membranes during pilot runs over a period of 1500 hours has not been great. Membrane pair resistance at the beginning of runs, for example, only increased about 5 percent even though fouling conditions during some runs were severe. Current efficiency, that is the fraction of the current that results in demineralization, has not changed significantly. Serious membrane damage would result in decreased current efficiency.

To obtain better control of turbidity and more dependable operation than was possible with the diatomaceous earth filter, a chemical clarification system has recently been installed before the carbon columns. This system consists of an upflow clarifier and dual media filters. Lime has been chosen for use in the clarifier because of the softening, phosphate removal, and alkalinity removal that this material offers. This change in pretreatment has not eliminated membrane fouling. The fouling rate is roughly the same as was obtainable with the diatomaceous earth filter when it was producing water of less than 0.1 JTU water.

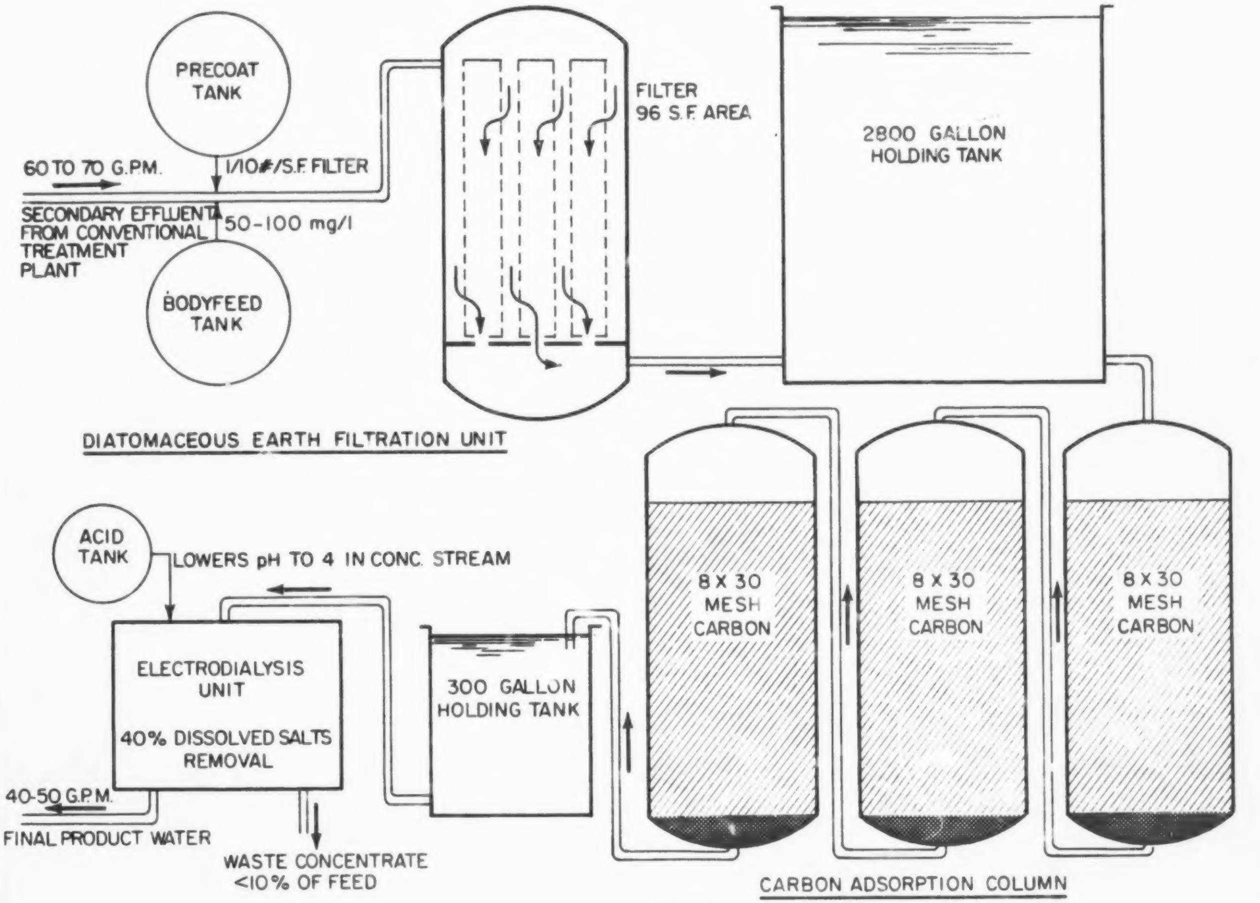
PRECOAT TANK
60 TO 70 G.P.M.
1/10#/S.F. FILTER
SECONDARY EFFLUENT FROM CONVENTIONAL TREATMENT PLANT
50-100 mg/l
BODYFEED TANK
FILTER 96 S.F. AREA
2800 GALLON HOLDING TANK
DIATOMACEOUS EARTH FILTRATION UNIT
ACID TANK
LOWERS pH TO 4 IN CONC. STREAM
ELECTRODIALYSIS UNIT
40% DISSOLVED SALTS REMOVAL
40-50 G.P.M.
FINAL PRODUCT WATER
WASTE CONCENTRATE <10% OF FEED
300 GALLON HOLDING TANK
8 X 30 MESH CARBON
8 X 30 MESH CARBON
8 X 30 MESH CARBON
CARBON ADSORPTION COLUMN

FIGURE 2. ELECTRODIALYSIS PILOT PLANT WITH DIATOMACEOUS EARTH FILTER PRE-TREATMENT LEBANON, OHIO

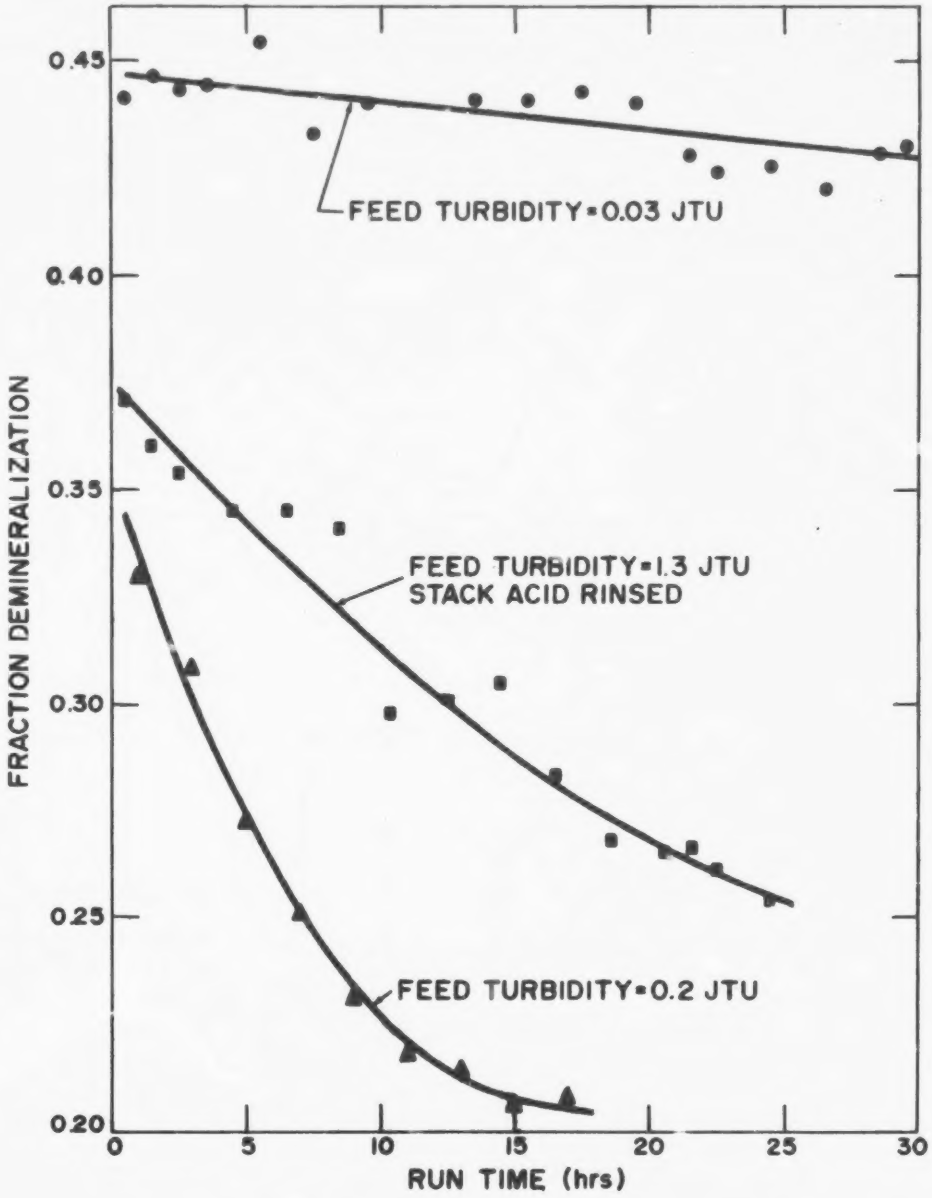

FIGURE 3. EFFECT OF TURBIDITY ON DEMINERALIZATION.

Further work with chemical clarification will be carried out.

C Other Investigations

Ionics Incorporated has operated a small pilot electrodialysis stack at Orange County on trickling filter effluent that had been alum clarified, chlorinated, and treated with granular activated carbon. In addition the stack had before it 10 and 3 micron cartridge filters and an ultraviolet light for sterilization. The fouling rate apparently was considerably lower than observed during operation of the Lebanon stack. Operation was halted after more than 800 hours of run time when a serious stack resistance increases occurred.

More recently this same electrodialysis system, including cartridge filters and ultraviolet light, has been operated on carbon treated, chlorinated secondary effluent at Pomona California. Here carbon treatment is carried out without any clarification. Frequent replacement of the cartridge filters is necessary. Preliminary results suggest that fouling will be at a lower rate than observed on the Lebanon stack. Further work is required to verify the early results and to determine the effect of the cartridge filters and ultraviolet light.

V APPLICATION TO BRACKISH WATER

The principal use for electrodialysis has been in treatment of brackish waters. These are inland waters containing enough salts to prevent or limit direct use. The mineral content is considerably less than for sea water, often about 2000 mg/l, and their compositions can vary widely from one location to another. Electrodialysis has been found practical for demineralizing these waters to 500 mg/l TDS or slightly less.

There are problems associated with brackish water treatment some of which are different from those observed in wastewater treatment. Fouling is sometimes troublesome, and is often not of organic origin. Instead inorganic materials such as traces of iron and manganese can cause the difficulty. It is usually considered necessary to remove essentially all the iron and manganese from ground water to be treated by electrodialysis. Scaling is often a problem because of high concentration of materials of low solubility such as calcium sulfate and calcium carbonate. To avoid scale formation the amount of concentrate waste is kept considerably higher than is possible in wastewater treatment. Often the volume of concentrated waste is from 33 to 100 percent of the volume of treated water.

There is an increasing number of electrodialysis installations using brackish water in the United States. Two of these are particularly well known. They are at Webster, South Dakota and Buckeye, Arizona. The Webster plant began operation in 1962 as a Demonstration Plant by the Office of Saline water and has a nominal capacity of 250,000 gpd. Electrodialysis equipment was supplied by the Asahi Chemical Industry Company of Japan. The feed water is not unusually high in TDS for brackish water since it contains only about 1700 mg/l. It is, however, a very difficult water to treat. It is high in calcium, sulfate, and bicarbonate so that scale formation is a serious problem. The water also contains significant amounts of iron and manganese that must be removed by using potassium permanganate injection and filtration through manganese zeolites before electrodialysis treatment. One of the wells that was to provide part of the feed water contains organic materials that cause a rapid increase in stack resistance. Many problems have arisen, therefore, during operation of this plant. These have been described in detail in a number of Office of Saline Water publications and summarized in a 1965 paper (4). As a result of the problems the Webster site has been used to test a number of pretreatment methods, both for iron and manganese removal and softening. An interesting feature of the plant as now operated is the use of periodic polarity reversal to reduce scale formation. Improved operation is obtained at a slight loss in current efficiency. Successful use of polarity reversal could represent a significant break-

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through in the application of electrodialysis to high-hardness, badly-scaling waters.

Results at Buckeye, Arizona have been more optimistic than results at Webster. The water, although higher in TDS, has a relatively large amount of sodium and chloride ions. Scaling is, therefore, much less likely to be a problem. The water contains no manganese and little iron. The equipment installed at Buckeye was supplied by Ionics, Inc. and has a design capacity of 650,000 gpd. Over the period October 1962, through June 1965, it is reported (5) that there were no major malfunctions. During that time the average load factor was only 32 percent. This unexpectedly low figure resulted partly from the recirculation of water through evaporative coolers. Recirculation was not possible with the more highly mineralized brackish water available before installation of the electrodialysis equipment and, therefore, the daily water consumption was higher. The low load factor has resulted in a higher than expected water cost when amortization of equipment is included, but the installation is, nevertheless, considered a success.

VI INDUSTRIAL APPLICATIONS

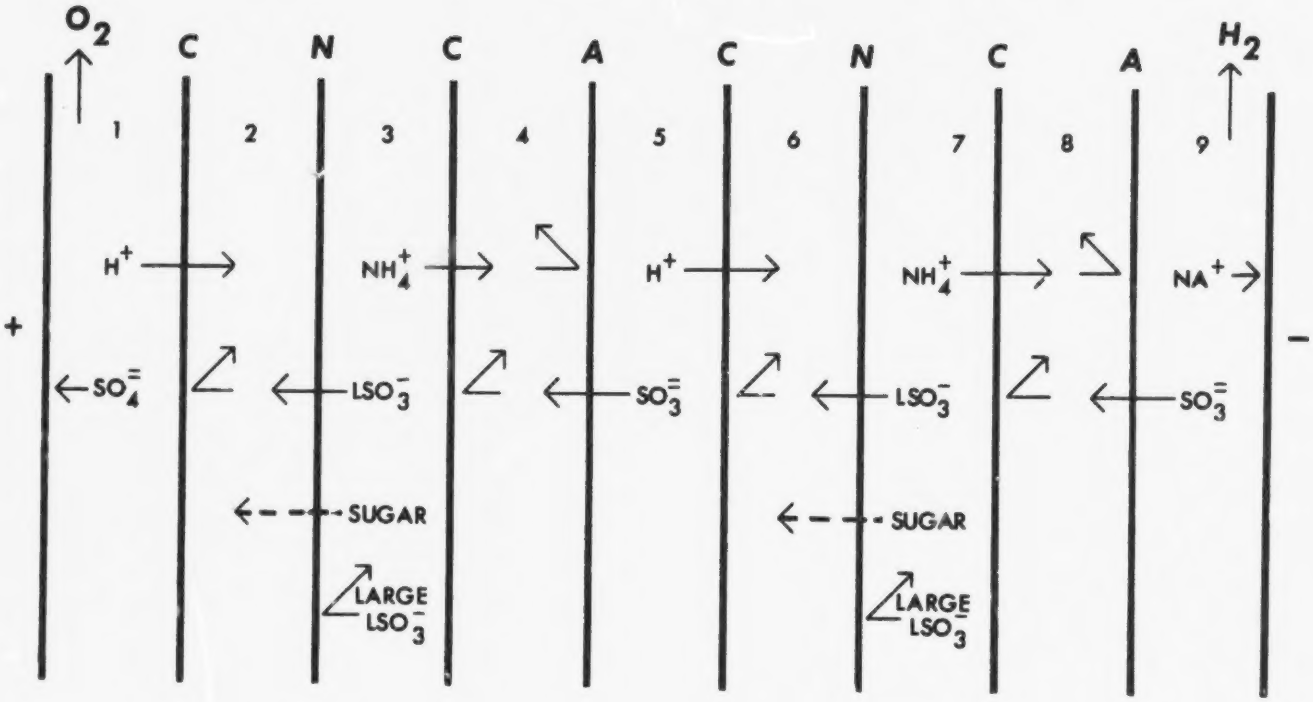
Use of electrodialysis for treatment of industrial wastes has been very limited. Two possible applications that have a pollution control aspect are treatment of pickle liquor and treatment of spent sulfite liquor. The first application is actually more nearly electrolysis than electrodialysis and results in recovery of iron and sulfuric acid from the waste (6). There is more interest in this process in Europe than in the United States. The second process was developed by the Sulfite Pulp Manufacturers Research League (7) and results in recovery of cations from the spent liquor. The principle of this modified electrodialysis process is shown in Figure 4. Spent liquor enters compartments [illegible] and [illegible] where cations and organics such as small ligno-sulfonate ions are removed. New liquor is made up in compartments 4 and 8. Compartments 5 and 9 serve as sources for sulfite ion. The spent liquor with low molecular weight organics removed may have a number of uses. The process operates at high current efficiencies and high current densities. Because of the arrangement of membranes, the anion membranes are protected from fouling by organics in the spent liquor.

Although electrodialysis has not yet been used extensively for treatment of industrial wastes, it may have wider application in the future. Its practicability is improved if useful materials can be recovered from the treatment. With the present cost picture for electrodialysis, recovery is probably a necessity. It is accomplished in the two examples cited above. There are undoubtedly many industrial waste streams where chemical recovery is a possibility.

In its basic form of alternating dilute and concentrate streams the process would ordinarily only be applicable to streams free of fouling soluble organics and suspended materials. By using special membrane arrangements such as in the sulfite liquor treatment, fouling problems can be reduced. It should be recognized that in applications where useful materials are recovered the added maintenance resulting from membrane fouling may not be prohibitive in cost.

The maximum concentration that can be economically treated would be limited to the brackish water range if by-product recovery were not possible. Electric power consumption for removing a large concentration of ions, ordinarily becomes prohibitive. Where useful materials are recovered the maximum concentration could be increased until the cost for electrodialysis exceeds the cost of other processes such as distillation. A detailed study of each particular application would have to be made to determine whether electrodialysis is practical.

There are two limitations to electrodialysis that may prevent its use in some applications. One limitation is the inability to practically remove ions below a concentration of several hundred mg/l. Where waste are very dilute, ion exchange should be more appropriate. The other limitation is the inability for the process to be very selective for any one material in a mixture. At present a valuable metal ion could not in general be removed


O_2
C
N
C
A
C
N
C
A
H_2
1
2
3
4
5
6
7
8
9
+
−
H^+
NH_4^+
H^+
NH_4^+
NA^+
$SO_4^=$
LSO_3^-
$SO_3^=$
LSO_3^-
$SO_3^=$
SUGAR
SUGAR
LARGE LSO_3^-
LARGE LSO_3^-

C—CATION SELECTIVE MEMBRANE
A—ANION SELECTIVE MEMBRANE
N—NON—SELECTIVE MEMBRANE

Figure 4. Electrodialysis Process for Treating Spent Sulfite Liquor

with high selectivity from common ions such as sodium and calcium. Relatively little work has been done to develop selective systems, however, and improvements are likely if a strong need arises. Again ion exchange may be a more practical form of treatment.

VII ULTIMATE DISPOSAL OF CONCENTRATED WASTE

Experience in the use of electrodialysis on municipal wastewater indicates that the volume of the concentrated waste will be 5 to 10 percent of the product volume. To prevent pollution of surface waters by this highly mineralized waste it must either be transported to the sea or in some other way be treated for disposal. Disposal, no matter what the method, will not be insignificant in cost except near the sea. For brackish water the potential disposal problem is also great. Presently the treatment of brackish water is limited enough that disposal of brine has not been a serious problem. Industrial waste treatment would not prevent a significant disposal problem if recovery of by-products from the concentrated waste were practiced. In that case the waste would be further treated anyway. If recovery were not possible, disposal or treatment of the concentrate to make it innocuous would be necessary. The volume of concentrate would vary widely depending upon the particular waste. If it is low in membrane scaling materials the volume may be only a few percent of the product. Each case must be considered separately.

VIII EQUIPMENT DESIGN

Since electrodialysis is a recently developed process, design of equipment is not yet highly sophisticated. The major American manufacturer, for example, has available a limited number of stack configurations to be used primarily for brackish water. Minor modifications are made in the equipment to adapt it to other uses. It would be a fortunate coincidence if obtainable equipment were the optimum for any given application. Because of the limited market, manufacturers have not been able to justify the extensive research and development work that is required for optimized design.

Several discussions of equipment design have been published (8, 9). Application of the methods were also demonstrated for the case of municipal wastewater (2). The reader is referred to these publications for details. In principle, these methods depend upon Ohm's Law and Faraday's Law and material balances. The resulting equations allow membrane area and power requirements to be calculated. Before making design calculations, it is necessary to know membrane resistances and limiting current density. These are empirical quantities, but manufacturers should have the necessary data available for their particular stack configurations and for brackish water feeds. Experimental data might be required for design of equipment to treat an industrial waste.

One serious fault with published design methods is that they do not emphasize the design of membrane spacers. After the designer chooses an available spacer and has the necessary empirical data it is relatively easy to size the equipment and determine power requirements. Optimum design of a spacer is a much more difficult problem. Presently, spacers range in form from rather open types that give low velocity and pressure drop to tortuous path types that give high velocity and pressure drop. To reduce production costs, manufacturers tend to pick one type and use it for all applications. The Office of Saline Water is presently sponsoring work on spacer design. Preliminary results suggest that even the brackish water spacers may be improved significantly. Further work is obviously justified.

At the present time, the user of electrodialysis equipment usually depends heavily upon the limited number of manufacturers for the ultimate design of a system. The number of types of stack components available is small. Use of the equipment is not yet so widespread that consulting engineers are experienced enough to undertake design themselves. If the market increases substantially, the situation will change. Not only will a greater variety of components become available, resulting in more flexibility of design, but the designing itself will be done by a greater number of people.

IX ELECTRODIALYSIS COSTS

A Capital Costs

When discussing the capital cost of electrodialysis, distinction must be made between present and projected costs. The market for this equipment has not expanded to the point where mass production of components is possible. The costs of membranes and spacers especially are very high. Capital costs do not represent, therefore, the minimum that would be possible just from an increased market and the competition that should develop.

It is difficult to make capital cost estimates without consulting a manufacturer. There is not sufficient information available in published form to make the precise estimates possible. Ionics, Inc. has at various times made available in company literature plant costs for their equipment as a function of capacity and feed concentration assuming the feed to be brackish water and product to contain 500 mg/l TDS. Table 1 shows some typical costs. These figures do not include pretreatment beyond a protective cartridge filter. Cost is strongly affected by both feed concentration and capacity. An independent cost estimate has been made for treatment of secondary effluent based partly upon experience from pilot operation. For a 10-mgd plant and using Ionics equipment, the estimated installed cost is $0.34/gpd. This is significantly higher than the Ionics estimate for 900 mg/l brackish water to which it should most closely compare. Much of the difference can be accounted for in the conservative feed rate per cell pair that was chosen for the wastewater estimate. A small amount was contributed by the inclusion of pH control equipment on the concentrate streams. This equipment is not usually supplied for brackish water treatment, but is desirable on wastewater treatment where there can be frequent changes in alkalinity.

The Office of Saline Water has, in the past, supported work on a procedure for estimating the cost of electrodialysis applied to brackish water. More recently, work was done on optimization of the process. This work will appear in publications from that organization.

B Operating Cost

Long term operating costs for electro-

Table 1

Investment Cost for Electrodialysis Plants

Plant Capacity (mgd)	Feed Concentration (mg/l)	Installed Plant Cost ($/gpd)
2	900	0.33
2	3,000	0.69
10	900	0.19
10	3,000	0.39
100	900	0.11
100	3,000	0.25

dialysis are available from only a few brackish water installations. Estimates are usually based upon experience combined with assumptions about long term maintenance requirements. Membrane life is probably the most questionable factor. Usually a 20 percent replacement per year is assumed. Pilot experience on wastewater suggests that membrane life is greatly affected by the care that is taken in handling the membranes and in operating the equipment. Although definite proof is not yet available, there is reason to believe that an annual 20 percent replacement may not be necessary. Ionics has estimated the cost of electrodialysis operation over a wide range of capacities and feed water concentrations. Some examples are given in Table 2. The estimates are for brackish water and assume 90 percent load factor and 20 percent annual membrane replacement. They include amortization of equipment. An independent estimate for the treatment of 10 mgd of wastewater was 16¢/1,000 gal. This is somewhat higher than the 12¢/1,000 gal for the nearly comparable 900 mg/l brackish water. The difference can be accounted for in the conservatively high capital cost estimate for the wastewater plant.

The effect of load factor on operating cost is significant. At the Buckeye, Arizona, brackish water plant, for example, it is estimated that at full load, the total cost of producing water should be 32¢/1,000 gal. The plant was actually designed to operate at a 48 percent load factor and produce water for 52¢/1,000 gal. For a number of reasons the load factor declined below the design value. For the first 32 months of operation it was only 32 percent. The result was a water cost of about 70¢/1,000 gal. This is an extreme example, but it points out the need to consider ways for minimizing fluctuations in flow. For industrial wastes, it may be possible to make extensive use of relatively cheap water storage to allow operation at a high load factor.

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2 Smith, J.D., Eisenmann, J.L., "Electrodialysis in Advanced Waste Treatment," Water Pollution Control Research Series Publication No. WP-20-AWTR-18.

3 Brunner, C.A., "Pilot Plant Experiences in Demineralization of Secondary Effluent Using Electrodialysis", presented at the 39th Annual Conference of the Water Pollution Control Federation, Kansas City, Missouri, Sept. 1966.

Table 2

Operating Cost for Electrodialysis

Plant Capacity (mgd)	Feed Concentration (mg/l)	Total Operating Cost ($/1,000 gal)
2	900	16
2	3,000	39
10	900	12
10	3,000	29
100	900	8
100	3,000	21

4 Calvit, B.W., Sloan, J.J., "Operation Experience of the Webster, South Dakota, Electrodialysis Plant", presented at the First International Symposium on Water Desalination, Washington, D.C., Oct. 1965.

5 Gillilard, E.R., "The Current Economics of Electrodialysis", presented at the First International Symposium on Water Desalination, Washington, D.C., Oct. 1965.

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REVERSE OSMOSIS

I INTRODUCTION

A The phenomenon of osmosis was first observed in the mid-18th century when studies were being made on biological membranes.

B It was noted that when two solutions of different concentration were separated by a semi-permeable membrane, the solvent would flow from the dilute to the concentrated side. A semi-permeable membrane is defined as one that will permit passage of some materials (usually a solvent) while rejecting others.

C The first experiments with artifically-prepared membranes were conducted in the mid-19th century when a membrane was made by precipitating copper ferrocyanide in the pores of porcelain.

D By 1920, interest in osmosis waned and, except for its biological importance, it was considered a laboratory curiosity.

E Developments in the last ten years by C.E. Reid and others of the University of Florida and S. Loeb and others at UCLA showed that the process can be reversed by applying pressure to the higher concentration side and that it has potential as a process for recovering reuseable water from a contaminated or saline source.

II THEORY

A Figure 1 illustrates the principle of osmosis and reverse osmosis. At equilibrium, the pressure on the more concentrated solution is known as the osmotic pressure. This pressure is dependent entirely on the difference in concentration between the two solutions and is not a function of the type of membrane, provided it is semi-permeable.

B It is well known that the "activity" or "chemical potential" of a solvent decreases when in a solution. Thus, the activity of water in distilled water is greater than the activity of water in a salt solution. This greater activity is thought to be the driving force that, in normal osmosis, causes water to flow through the membrane. In brackish and sea water, this driving force is about 1 psi for every 100 ppm salt in solution.

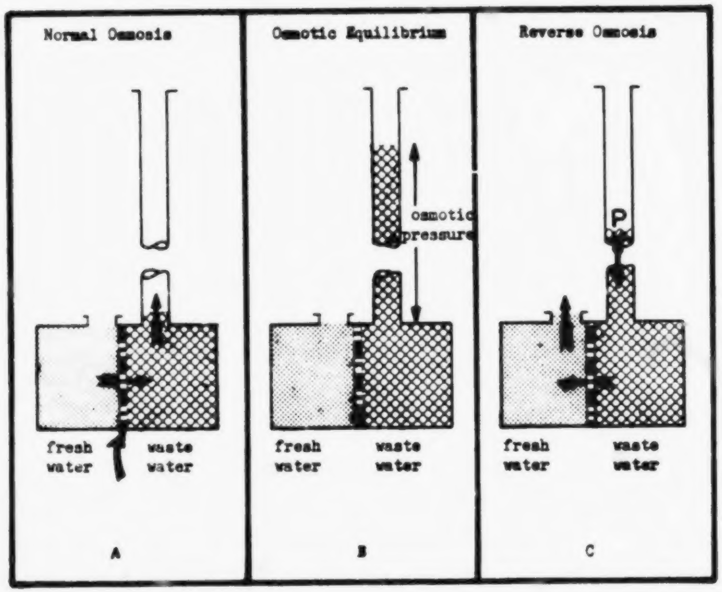
C The actual mechanism of transfer of water through a reverse osmosis membrane is not completely understood. The most generally-accepted theory is that water passes through the membrane by successive transfer from one adsorption site to the next. In the case of cellulose acetate, the most common membrane material, the adsorption forces arise from hydrogen bonding.

D The rate of transfer of water through a membrane in reverse osmosis is directly proportional to the applied pressure minus the osmotic (back) pressure and inversely proportional to the thickness of the membrane. Increasing temperature, since it raises the activity of the water, will result in a greater water flux through the membrane.

E As stated before, the flux of water is directly proportional to the pressure driving force. The flux of salt, however, is a function only of the salt concentration. Raising the applied pressure, therefore, reduces the salt content of the product.

III MEMBRANES AND THEIR MANUFACTURE

A Reverse osmosis was first made practical by the discovery (by Dr. Loeb and co-workers at UCLA) of a process for making a cellulose acetate membrane with a very thin active layer. These membrane are about 100 microns in total thickness. The active, dense layer that transmits the


Normal Osmosis
Osmotic Equilibrium
Reverse Osmosis
osmotic pressure
P
fresh water
waste water
fresh water
waste water
fresh water
waste water
A
B
C

315-63-77

THE PRINCIPLE OF REVERSE OSMOSIS
(WASTE WATER)
Figure 1

water and rejects the salt is only 0.25 microns thick - the rest is a spongy back-up material that has little, if any, desalination properties.

B A typical formulation for making cellulose acetate membranes is shown in Table 1.

TABLE 1

CASTING SOLUTION FOR CELLULOSE ACETATE REVERSE OSMOSIS MEMBRANES

Material	Weight
Cellulose Acetate	22.2
Magnesium Perchlorate	1.1
Acetone	66.7
Water	10.0

This casting solution is poured on a glass plate and its thickness is adjusted by a doctor blade. The plate is then immersed in ice water for 30 to 60 minutes during which essentially all of the magnesium perchlorate is removed from the membranes. The membrane is then immersed in hot water for 3-10 minutes. The water temperature is critical - from 55°C on up, the salt rejection properties are improved at the expense of flux through the membrane. Continuous casting procedures have been developed but they are proprietary and nothing has been published on them.

C The degree of acetylation of the cellulose is an important factor. The optimum membrane is produced from cellulose acetate containing about 2.5 acetate groups per cellulose molecule. The tri-acetate is produced and it is hydrolyzed to the 2.5 level. Further hydrolysis degrades the membrane - this is controlled in service by maintaining the pH of the feed water at about 5.5.

D Compression of the spongy under-layer at the elevated pressures necessary during operation results in flux decline. Efforts are underway to produce a thin (0.25 micron) dense layer that could be put on a porous, non-compressible substructure.

E Considerable effort has been and is being expended on the development of new membrane materials. As yet, none of those investigated has proven as effective as cellulose acetate. Some of the more promising materials studied to date include poly (vinylene carbonate), polyvinylpyrollidone and graphitic oxide.

F A recent development in this field has been made at the Oak Ridge National Laboratories of the Atomic Energy Commission. Dr. Kraus and co-workers have developed a dynamically-formed membrane having permeation rates of 100-300 gallons/day ft^2 (gfd) compared to a typical rate for cellulose acetate of 20-30 gfd.

1 The rejecting layers are formed by pumping water containing a hydrous oxide (zinconium or thorium) or a polyelectrolyte [poly (vinylbenzyl-trimethyl-ammonium chloride)] over a porous body.

2 The porous body can have a pore size up to 5 microns in diameter.

3 Salts containing polyvalent counter-ions (Mg^{+++} or $SO_4^{=}$) are poorly rejected and destroy the rejection capacity of the membranes for mono-valent salts.

IV ENGINEERING OF REVERSE OSMOSIS UNITS

A Several different designs have been proposed to meet the design objective of producing the maximum amount of quality product per unit cost.

1 The "flat plate" membrane configuration is similar to a plate and frame filter press. These units have been tested extensively on brackish- and sea-water but little work has been done on wastewaters.

2 The spiral-wound membrane is illustrated in Figures 2 and 3. The objective of this design is to increase the surface area to volume ratio. This configuration has been evaluated on brackish- and sea-water and is being evaluated on wastewater at the FWPCA Pomona, California pilot plant.

3 The tubular unit is shown in Figure 4. Another form this can take is that of a metal tube with weep-holes drilled for delivery of the product water.

4 The newest configuration consists of hollow fibers with water passing from the outside to the inside of the fibers. Figure 5 shows a schematic of such a unit.

B Two different concepts have been employed in the design of these units. The first three described above depend on relatively high permeation rates (20 gfd). The hollow fiber units rely more on very high surface area per unit volume with low permeation rates (0.15 gfd).

C Equipment must be designed to minimize the "boundary layer" effect - that is, the existence of a high concentration layer at the membrane surface. This problem is related to the permeation rate, becoming more severe as the rate increases.

D Rapid membrane replacement and inexpensive pressure construction are also goals of the designers in this field. Membrane life is still an unknown quantity, particularly in wastewater treatment, so configurations in which membrane replacement is costly could be impractical.

V LABORATORY INVESTIGATIONS ON WASTEWATER

A Aerojet-General conducted a 1-year study on the application of reverse osmosis to wastewater. The equipment consisted of two 0.5 ft^2 membranes in series (flat-plate). The concentrate stream was returned to the feed tank to determine the effect of increasing concentration. The principal findings are listed below.

1 The product quality was excellent. Table 2 shows the product quality from two test runs.

2 Water flux through the membrane decreased rapidly. Acid addition to the feed to maintain a pH of 5 minimized this problem but flux reduction with time was still severe.

3 After a period of several hours, the flux at 1500 psi feed pressure was about the same as that obtained at 750 psi.

4 The flux through "loose" membranes, though high originally, rapidly declined to the same level as the "tight" (low flux, high salt rejection) membranes.

5 Removal of organics from the feed by carbon adsorption was helpful in reducing the rate of flux decline.

6 Test results showed that biological attack of the membrane could be a severe problem.

B The General Atomic Division of General Dynamics ran several spiral-wound modules on wastewater at the Pomona Water Renovation Plant of the Los Angeles County Sanitation Districts. This was a continuous flow-through operation recovering about 5% of the feed as product.

1 Water quality was again excellent as can be seen in Table 3. The "A" modules contained "tight" membranes, the B - "loose" membranes and the "C" - intermediate.

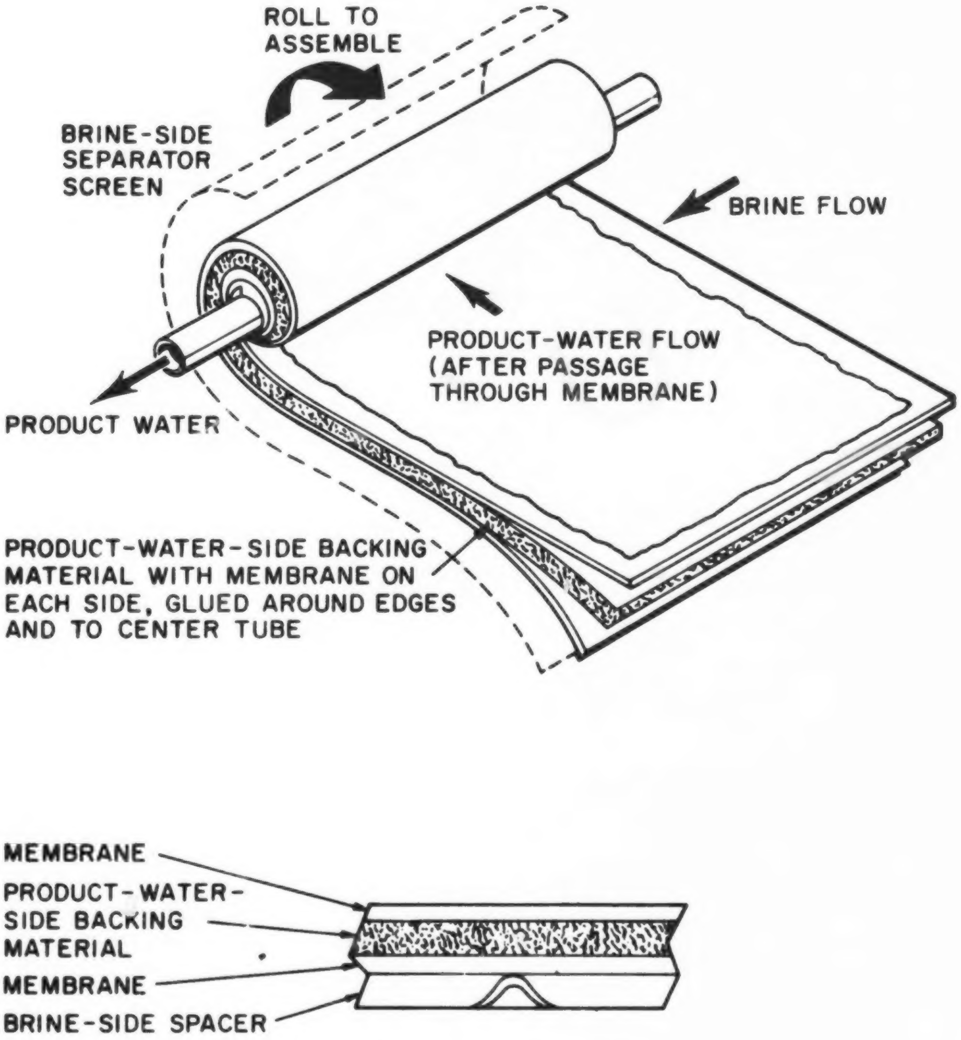

ROLL TO
ASSEMBLE
BRINE-SIDE
SEPARATOR
SCREEN
BRINE FLOW
PRODUCT-WATER FLOW
(AFTER PASSAGE
THROUGH MEMBRANE)
PRODUCT WATER
PRODUCT-WATER-SIDE BACKING
MATERIAL WITH MEMBRANE ON
EACH SIDE, GLUED AROUND EDGES
AND TO CENTER TUBE
MEMBRANE
PRODUCT-WATER-
SIDE BACKING
MATERIAL
MEMBRANE
BRINE-SIDE SPACER

Figure 2. A Spiral-Wound Reverse Osmosis Module

Reprinted with permission from General Dynamics,General Atomic Division

GENERAL DYNAMICS
General Atomic Division

100,000 GALLONS PER DAY WATER TREATMENT PLANT

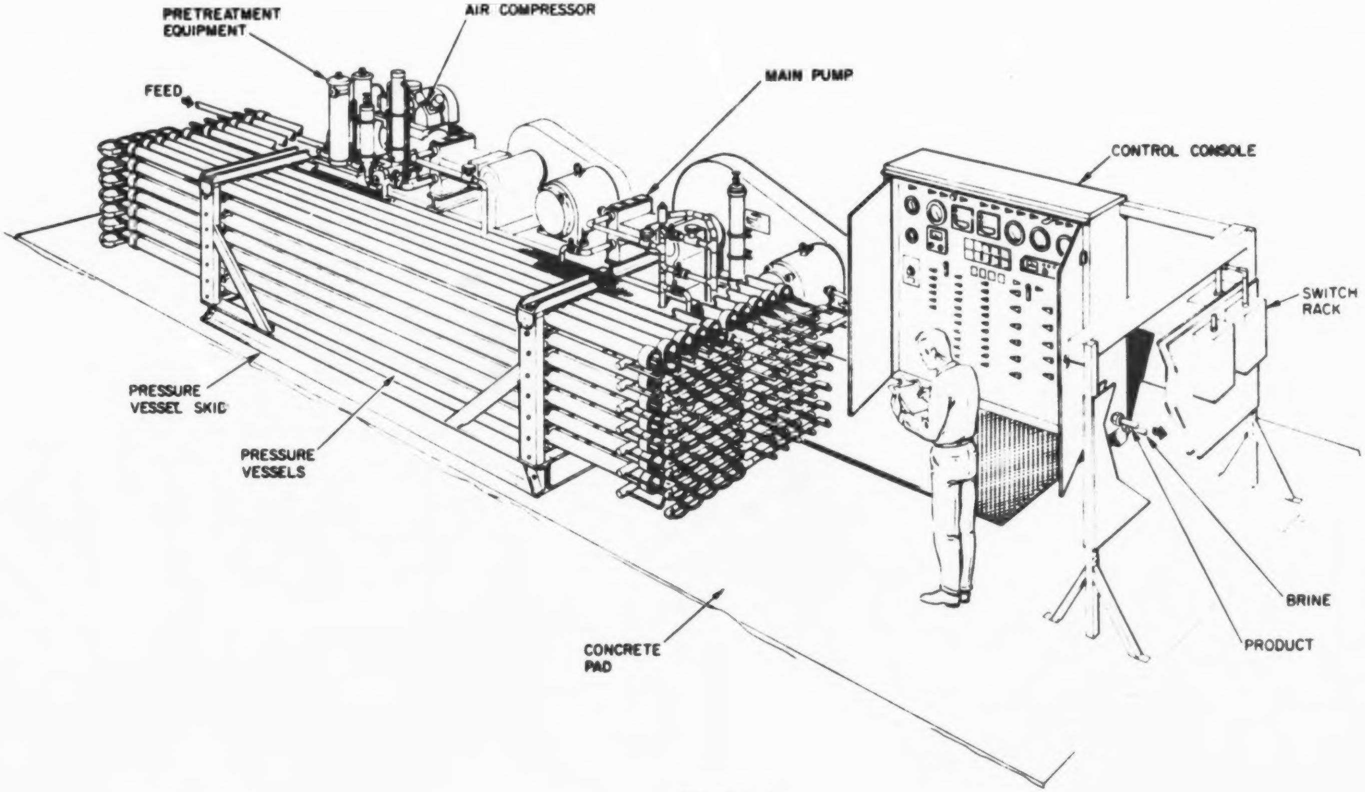

PRETREATMENT EQUIPMENT
AIR COMPRESSOR
FEED
MAIN PUMP
CONTROL CONSOLE
SWITCH RACK
PRESSURE VESSEL SKID
PRESSURE VESSELS
BRINE
PRODUCT
CONCRETE PAD

Figure 3

5005-MD-60

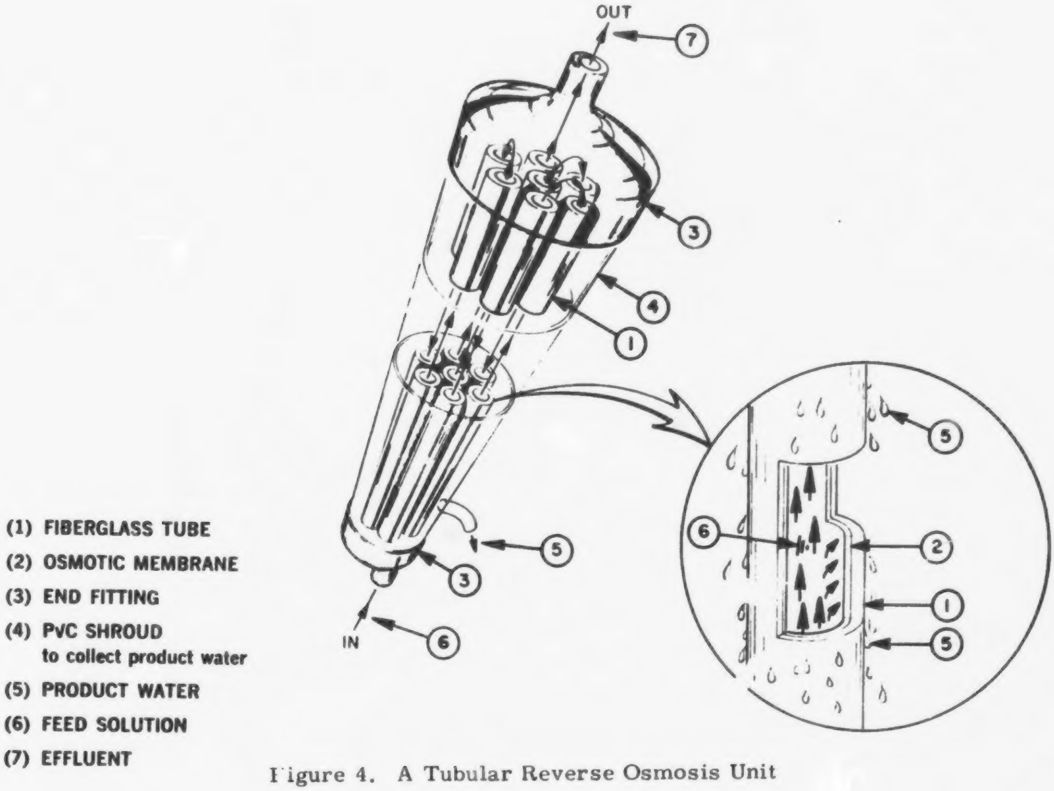

OUT
⑦
③
④
①
⑤
⑥
②
①
⑤
⑤
③
IN
⑥
(1) FIBERGLASS TUBE
(2) OSMOTIC MEMBRANE
(3) END FITTING
(4) PVC SHROUD to collect product water
(5) PRODUCT WATER
(6) FEED SOLUTION
(7) EFFLUENT

Figure 4. A Tubular Reverse Osmosis Unit

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2 As before, the "loose" (high flux-low rejection) membranes plugged fastest and were soon delivering no more than the "tight" membranes.

3 Flux decrease was still a problem, ranging from 25% in 1500 hours for the tight membranes to 86% in 290 hours for the loose membranes.

C Similar work was done on a spiral unit by the New Jersey Department of Health and others on a sewage plant effluent and on water from the Hackensack River. Results were similar. Bacteriological removals were determined during this study and the MPN reduction/ range was from 80 to 99.9%.

VI PILOT INVESTIGATION ON WASTEWATER

A The only pilot investigation on wastewater of reasonable duration has been conducted at the Pomona pilot plant on a 5000 gpd unit utilizing the spiral membrane configuration.

B The first year of operation was plagued by operating difficulties and no encouraging results were obtained. The more significant problems are listed below.

1 Some of the feed by-passed the membrane module, going between the outside of the module and the pressure casing. This caused a flow decrease through the feed channel, thus accentuating the boundary-layer effect.

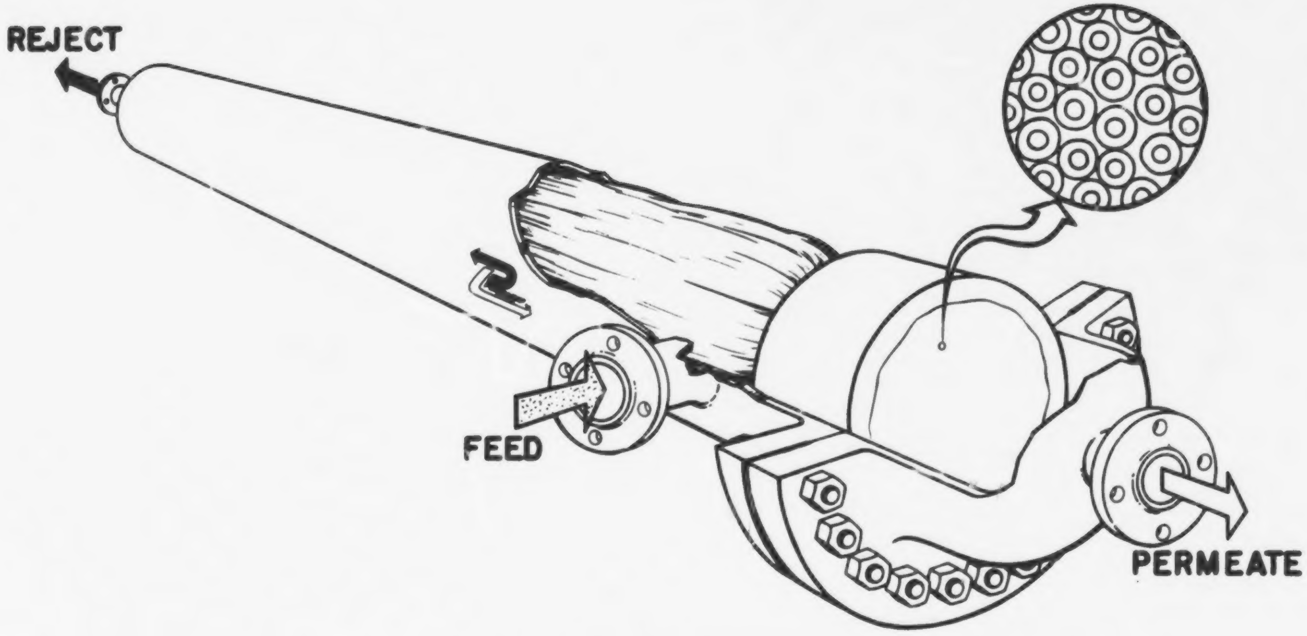
REJECT
FEED
PERMEATE

Figure 5. A Hollow-Fiber Reverse Osmosis Unit

Reprinted with permission of E.I. du Pont de Nemours and Company

TABLE 2

WATER MINERAL ANALYSIS

	Feed Water (Typical) ppm	Product (Test 18) ppm	Product (Test 28) ppm
TDS	550	15	28
ABS	4.5	0.1	0.1
COD	95	2	6.0
pH	5[1]	6.3	5.5
Cations			
Na^+	85	4.6	6.1
K^{++}	40	4.9	2.7
NH_4^+	25	0	3.9
Ca^{++}	125	0	2.6
Mg^{++}	50	0.7	0
Fe^{++}	N. D.	0	0
Anions			
Cl^-	65	20.3	22.1
NO_3^-	2	0	0
HCO_3^-	260	8.1	3.5
$CO_3^=$	0	0	0
$SO_4^=$	200	1.7	3.3
$SiO_3^=$	30	2.9	2.9
$PO_4^=$ (total)	25	0	0

N.D. - not determined

[1] pH adjusted during test

TABLE 3. PRODUCT QUALITY - REVERSE OSMOSIS TREATMENT OF WASTEWATER

	Feed Water*	Product From Module 1-6-3 5A1 **	Product From Module 3-24-1 3B2 **	Product From Module 1-22-1 5C2 **
Alkalinity, ppm $CaCO_3$	213	< 25	88	37
Ammonia Nitrogen, ppm N	11.2	2.8	7.0	3.5
Total Nitrogen, ppm N	12.6	2.8	7.4	3.5
Specific Conductance, µmhos/cm	933	60	399	215
Chloride, ppm Cl	92	4	68	32
Hardness Total, ppm $CaCO_3$	195	3.8	27.4	6.1
Phosphate Total, ppm PO_4	5.6	0.2	2.2	0.4
Potassium, ppm K	17.8	1.2	10.4	5.0
Sodium, ppm Na	107.2	7.5	63.0	38.5
Calcium, ppm $CaCO_3$	138	2.8	20.3	3.8
Magnesium, ppm $CaCO_3$	58	1.4	7.1	2.3
Dissolved Solids, ppm	531	28	224	118
Sulfate, ppm SO_4	71.4	5.3	2.1	3.9
Fe, ppm Fe	0.10	0	0	0
ABS, ppm	3.8	< 0.1	1.1	<0.1
COD, ppm O	41	4	8	4
pH	7.2	6.6	7.1	6.7

*Chlorinated and diatomaceous earth filtered secondary effluent.

**Pressure = 205 psi
Temperature = 70°F
Time in Use = 1464 hours for 1-6-3 (5A1)
160 hours for 3-24-1 (3B2)
975 hours for 1-22-1 (5C2)

2 The modules tended to "telescope" in the direction of flow due to pressure drop through the feed channels.

3 pH control was erratic and the control set-up was such that the feed pump would shut down when pH control was lost. The pressure surge caused by this sudden loss of pressure accentuated the telescoping and ripped apart some of the taped joints holding the module together.

4 Solids build-up in the feed channels raised the pressure drop through the unit. Calcium sulfate and biological solids were the principal sources of trouble.

C From late June until late September of 1967, the unit has been operating satisfactorily. The feed water was carbon-treated secondary effluent rather than untreated secondary effluent as before.

In addition, pH control was switched from sulfuric to hydrochloric acid and 5 ppm chlorine was added to the feed. The results have been most satisfactory, as listed below.

1 We are operating at a feed rate of about 4800 gallons per day and recovering 83% of the feed as product. The flux rate is 5 gfd at a pressure of 400 psi and there has been no significant decline in flux in 2000 hours of operation.

2 A special anti-telescoping device installed by General Atomic has been successful in overcoming this problem.

3 Product quality has remained high as shown by Table 4. Table 5 shows gradual degradation of product quality between start-up and after 2000 hours on-stream. These increases are probably due to slight pin-hole leaks developing in the membranes.

4 Daily flushing with an air-tap water mixture has been successful in removing any particulate material that accumulates or forms in the modules.

D The study program for the future at Pomona calls for: 1) another attempt at feeding secondary effluent instead of carbon-treated water, 2) using sulfuric rather than hydrochloric acid for pH control, and 3) increasing the operating pressure to obtain 90% recovery of feed.

Table 4. WATER QUALITY DATA FROM GENERAL ATOMIC REVERSE OSMOSIS UNIT

Tube No.	PO_4 (mg l)		COD (mg l)		NH_3-N (mg l)		NO_3-N (mg l)		TDS	
	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range
Feed	30.9	21.6 - 37.8	10.8	6.7 -14.4	9.2	2.5 - 26.0	2.4	0.8 - 5.0	623	530 - 748
1A	0.22	.09 - .53	1.2	0.0 - 2.3	1.3	0.6 - 2.0	0.4	0.0 - 0.8	51	0 - 113
1B	0.16	.05 - .35	1.1	0.0 - 2.6	1.2	0.5 - 2.2	0.5	0.0 - 0.8	36	9 - 85
2C	1.4	1.3 - 1.5	2.4	0.4 - 6.2	2.8	0.7 - 7.3	0.9	0.4 - 1.7	60	
3C	1.1	.07 - 3.4	1.6	0.0 - 3.6	1.8	1.0 - 2.6	0.7	0.0 - 1.6	70	14 - 173
4C	0.43	.07 - 1.1	1.8	0.6 - 4.0	1.7	0.9 - 2.6	0.9	0.4 - 1.6	67	22 - 120
5C	0.48	.08 - .90	2.0	0.0 - 5.0	1.7	1.1 - 2.6	0.9	0.4 - 1.[illegible]	53	35 - [illegible]
6C	0.41	.08 - 1.0	1.6	0.0 - 3.6	1.8	1.0 - 3.1	1.0	0.7 - 1.6	53	6 - 113
7C	0.37	.04 - 1.8	2.3	0.0 - 6.1	2.6	1.3 - 4.6	1.0	0.[illegible] - 2.4	67	34 - 136
8C	0.77	.07 - 1.8	2.4	0.0 - 5.0	3.2	1.8 - 5.3	1.6	0.6 - 2.6	95	36 - 196
Total Product	0.57	.13 - 1.2	1.7	0.0 - 3.4	1.7	0.9 - 3.4	0.8	0.4 - 1.2	73	30 - 113
Brine	177.	73. -240.	43.8	26.6 -60.4	94.	19. -240.	7.5	2.8 -13.7	3402	2861 - [illegible]
% Reduction	98.2		84		82		67		88	

TABLE 5. PRODUCT WATER CONDUCTIVITY - GENERAL ATOMIC REVERSE OSMOSIS UNIT

Tube No.	Initial Cond. (μmhos/cm)	Present Cond. (μmhos/cm)
1A	50	80
1B	50	80
2C	100*	140
3C	70	200
4C	70	110
5C	75	110
6C	85	120
7C	90	220
8C	110	250

Feed Conductivity: Before acidification: 800
After acidification: 950

Brine Conductivity: 4000

*High due to use of several modules with slight leaks

VII COSTS

A Reverse Osmosis is in an early stage of development and, as could be expected in this stage, there is a wide range on estimated costs. Different manufacturers have estimated costs for a 10 mgd plant ranging from $0.25 to over $1.00/1000 gallons. Some of the factors that will determine the cost of a reverse osmosis system for wastewater renovation are listed below:

1 Flux through the membranes is the prime factor affecting costs. Most cost estimates have been based on an optimistic flux of 20-30 gfd.

2 Membrane life is also an important cost consideration. If the membrane life is short, the reverse osmosis unit will have to be designed so that membrane replacement is rapid and inexpensive. This is an approach being taken by some manufacturers.

3 The degree of pre-treatment necessary prior to entering the reverse osmosis cell will influence application of the process. If organic materials have to be removed before the membranes, then reverse osmosis is simply a demineralization process and must compete economically with electrodialysis and ion exchange.

4 The product to waste ratio obtainable with reverse osmosis is an important consideration. If 90% of the feed is recovered as product, the cost of disposing of the concentrate stream by injection into deep wells (providing the geology is appropriate for this) would be about 2¢/1000 gal. of water produced. If only 80% of the feed can be recovered, the cost of disposal will be 5-6¢/1000 gallons.

5 The production rate of membrane materials will affect the cost of the

operation. The raw material costs are almost negligible but the manufacturing costs are high. Membrane consumption must be high enough to support continuous, automated production facilities.

B Despite all these considerations, reverse osmosis could have widespread application in the future in locations where demineralization of wastewater is required for reuse or pollution control purposes. It must be remembered that reverse osmosis is still an "infant" when compared to processes such as distillation and carbon adsorption. The field is wide open and significant developments are occurring rapidly.

VIII FUTURE PLANS

A The FWPCA has plans for continuing support of development work in the reverse osmosis field, both in testing of new membrane materials and in improvements in engineering design.

B A major undertaking under consideration is the funding of work to determine the minimum pretreatment necessary to prepare a raw sewage for treatment by reverse osmosis. It seems most unlikely that conventional primary and secondary treatment provide the ideal conditioning of the wastewater for the membrane process.

C A major study funded jointly by the FWPCA and the Eastern Municipal Water District of Hemet, California is just getting underway. Starting with secondary effluent, several different types of reverse osmosis units will be run in parallel. Pretreatment of the secondary effluent by any combination of clarification, filtration and carbon adsorption will be possible.

IX INDUSTRIAL APPLICATIONS OF REVERSE OSMOSIS

A The Pulp Manufacturers Research League in Appleton, Wisconsin has investigated reverse osmosis as a method for solving both their water pollution and water supply problems. They hope to operate a 50,000 gpd plant that could be evaluated on several waste streams at a number of pulp mills. Laboratory investigations have been limited to short-term batch runs but the results appear promising.

B The Aerojet-General Corporation has received a grant for a study of the application of reverse osmosis to various industrial waste streams at the Odessa, Texas petrochemical complex. A 560 square foot unit will be mounted on a trailer that will also include a clarifier and diatomaceous earth filter to serve as pretreatment units. The objectives of the study will be to investigate the following factors:

1 Reliability of reverse osmosis as an industrial waste treatment process.

2 Sensitivity of the membrane performance to input water quality.

3 Membrane life.

4 Design data for large-scale units.

5 Economics of the process

Table 6 presents characteristics of some of the waste streams that will be fed to the unit.

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TABLE 6. ODESSA INDUSTRIAL COMPLEX WASTE WATER STREAMS

Stream	A	B	C	D	E	F	Combined Waste
Total Hardness	80-200 (130)	10-100 (40)	0-30 (15)	130-200 (150)	150-320 (200)	0-625	60-1700 (150)
Ca	21	25	0-8	45	109		20-150
Mg	6	3	0-2	3	8		2-30
Fe	2.5	1	3-5 (4)	7	2	1	<1.0-2.5
NH_3	2-15	1-15	40-125 (60)	0-50 (10)	0-13 (3)	4	1-25 (10)
Total Dissolved Solids	2250-2500	700-1150	4400	10,800	1550-1810	2300	3,500-25,000 (5000)
pH	8.5-9.5	8.5-11.5 (9.6)	9-12 (10)	6.5-7.5	6.5-8.0 (7.3)	8.5-12	8.5-10.0 (9.5)
(COD)	2300	770	2440-3715	140	45-80	1500-7500	650-800
Temperature, F	100-120	96-130 (110)	110-135	68-85	70-95	75-110 (85)	85-110 (90)

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ION EXCHANGE

I INTRODUCTION

Ion exchange is a well known method for softening water and for producing deionized water. It may also be practical for removing the inorganic materials added to water during use. Although ion exchange equipment is very different in form from electrodialysis equipment, the two processes have many similarities. Both have application over the same range of feed concentrations and have a number of similar operating problems. Ion exchange has greater capability for selective removal of particular ions down to very low concentrations. It is also capable of total demineralization. Chemical regeneration of ion exchange resins is less desirable than the continuous electrical regeneration that occurs in electrodialysis.

II PRINCIPLES

A Mechanism of Ion Exchange

Ion exchange materials are available as solids and liquids. Since the bulk of ion exchange applications presently use the solid ion exchange materials, these will be discussed here. Solid ion exchangers are adsorbents that can be thought of as having many ionic sites in their structure. To maintain electroneutrality each ionic site has associated with it an ion of opposite charge or counter ion. If the ion exchange material is contacted with a solution of ions different from the original counter ions, the latter can be replaced. The replacement of ions of one type by another is ion exchange. When all the original counter ions have been replaced the resin is exhausted. A concentrated solution of the original counter ion must be used to regenerate the ion exchanger.

Many kinds of materials, both synthetic and naturally occurring, have the capability to exchange ions. Synthetic organic resins, however, have replaced natural materials in some applications and will probably continue to do so in the future. The synthetic resins can be tailored better to meet the requirements of a specific application. There are four major types of ion exchange resins. These are strong and weak acid and strong and weak base. The names acid and base come from the fact that the counter ions associated with these resins may be hydrogen and hydroxyl respectively. Other names for acid and base resins are cation and anion resins. For many applications these last terms are the more appropriate.

Strong acid resins are commonly composed of sulfonated styrene and divinyl benzene. In the hydrogen form they can be used to remove other cations from solution. This is called salt splitting and is shown in the following equation:

$$RSO_3^-\ H^+ + Na\ Cl \longrightarrow RSO_3^-\ Na^+ + HCl$$

Regeneration would be the reverse of this reaction, probably using sulfuric acid. Acid in excess of the stoichiometric amount is required for good regeneration. Softening can also be carried out with these resins as follows:

$$2RSO_3^-\ Na^+ + Ca^{++} \longrightarrow (RSO_3^-)_2\ C_a^{++} + 2\ Na^+$$

After softening, sodium chloride is usually used for regeneration.

Weak acid resins often have carboxyl groups in their structure. These resins in the hydrogen form will not split salts, but will remove cations from solutions of weak bases as shown:

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2O + CO_2$$

In the hydrogen form these resins are not ionized. Less excess regenerant is required for these resins than for the strong acid resins.

Strong base resins have quaternary ammonium groups in their structure. They will split salts by exchanging hydroxyl ion for other anions as follows:

$$RN(CH_3)_3^+OH^- + NaCl \longrightarrow RN(CH_3)_3^+Cl^- + Na\ OH$$

This is not a common use, however, since salt splitting can more cheaply be carried out with strong acid resins. These resins are useful for removing the anions of weak acids formed after cation exchange. Regeneration is carried out with a strong base. Considerable excess regenerant is required.

Weak base resins contain various amine groups. In the base form these are not ionic and do not remove anions by ion exchange. They react with acids in solution, however, and in this way accomplish anion removal. A common use is in removal of the acids formed after cation exchange:

$$RNH_2 + HCl \longrightarrow RNH_3^+Cl^-$$

These resins will not remove most weak acids; a strong base resin after the weak base resin is required. Weak base resins can be regenerated with weak bases such as ammonia. Only a slight excess is required.

For an excellent discussion of resin types and detailed consideration of ion exchange rates and equilibria the reader is referred to the book by Helfferich (1).

B Conventional Method of Application

Most ion exchange operations use fixed columns of resin granules or beads. Usually the solution to be treated is fed down-flow through the column. As operation continues the resin becomes exhausted.

There is no sharp distinction, however, between fresh and exhausted resin. A schematic diagram of the degree of exhaustion along the column is shown in Figure 1 for exchange of sodium ion for hydrogen ion. It is assumed the resin was initially all in the hydrogen form. Before all the hydrogen ion is exchanged there will be a breakthrough of sodium ion. Regeneration must then be carried out. The resin is first backwashed to remove suspended material that may have collected. The exhaustion profile is disturbed by the backwash because of fluidization and mixing of the bed. Regeneration is then begun, usually in down-flow. If sufficient acid were used the resin could be restored completely to the hydrogen form. This is not possible, however, without using an impractical excess of regenerant. Ordinarily the resin would be regenerated until nearly all the resin at the top of the column was in the hydrogen form. Further down the column there would be an increasing fraction of the sodium form that leads to leakage of sodium ion when ion exchange is resumed. The amount of excess regenerant necessary depends upon the amount of leakage that can be tolerated. After regeneration the column is rinsed for thorough removal of regenerant from the interstitial liquid before being put back into use.

C Countercurrent Regeneration and Continuous Operation

Although the conventional method of operation can be made to give good results, it is not particularly economical. Regenerant requirements can be reduced substantially if countercurrent regeneration can be used. Consider, for example, what would happen in Figure 1 if regenerant were added in the opposite direction from the feed. The least exhausted resin would contact the most concentrated regenerant giving a greater concentration driving force than with cocurrent regeneration. As the regenerant continues through the bed it contacts resin that is more nearly exhausted. Although the regenerant concentration driving force at the feed end of the column is less than in the case of cocurrent regeneration, the driving force for the column as a whole is greater. The most highly regenerated resin occurs at the outlet of the column rather than the entrance as in cocurrent regeneration. This resin acts as a polish to reduce leakage of unwanted ions. Conventional operation would require excess regenerant to accomplish the same degree of leakage control.

If carried out in a single column, countercurrent regeneration requires that feed and regenerant enter the column at opposite

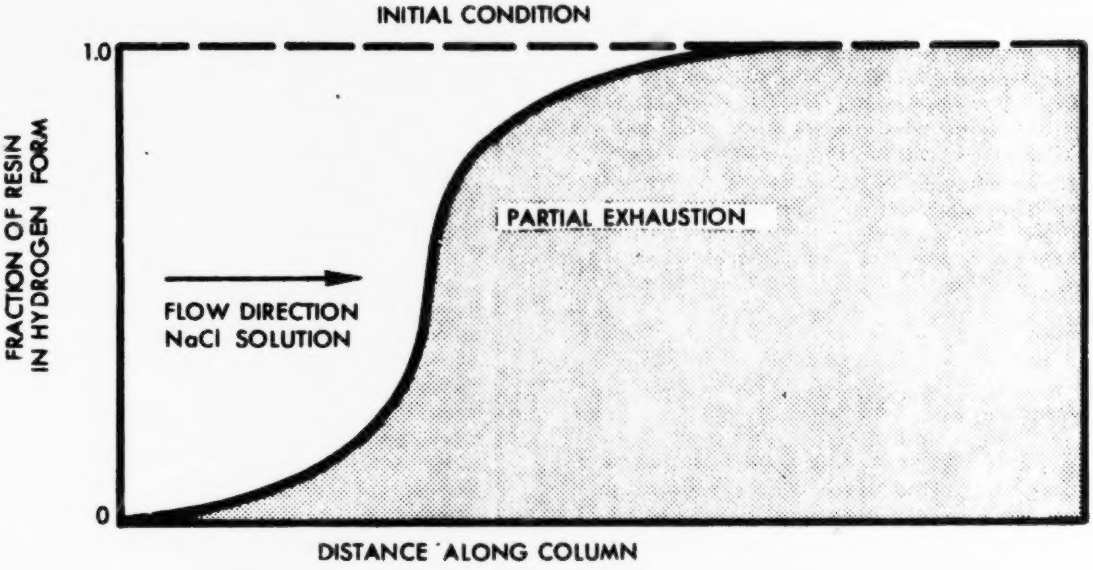

Figure 1. Effect of passing NaCl Solution through Cation Resin in the Hydrogen Form.

ends. By breaking the column into two or more sections in series it is possible to get some measure of countercurrent action even if downflow is used for both streams. It would be necessary, however, to regenerate the last section of column first and reuse the partially spend regenerant in each preceding column.

In some respects the most efficient type of operation is that obtained from continuous countercurrent treatment. In such a system, resin and raw water move continuously in opposite directions through a column with exhausted resin existing at the water entrance and regenerated resin entering at the water exit. The exhausted resin continuously enters a regeneration chamber where it is countercurrently contacted with regenerant. This system makes best use of resin capacity, gives minimum bed size and minimum regenerant requirements. Equipment costs are, however, higher than for fixed bed contractors. Mechanical problems can arise, in the resin-moving system. Several nearly continuous systems are in use, one of these being the Higgins Contactor (2).

D Mixed Bed Ion Exchange

When a cation exchanger in the hydrogen form is used to remove mineral cations from solution, there is a gradual buildup of hydrogen ion in the water down through the column. This tends to regenerate the resin and slows down the removal of the mineral cations. In the case an anion resin in the hydroxyl form the solution tends to become alkaline and again there is a slowing of exchange rate. If particles of the two types of resin are well mixed, however, demineralization will take place without significant pH shifts. The mixed bed type of operation is quite effective when highly demineralized water is required. There is a problem in regeneration, however, since the two types of resin must first be separated. By making the resins of different density or particle size separation can be achieved by backwashing at a high enough rate to fluidize the bed.

III PARTICULAR ION EXCHANGE SYSTEMS

A Strong Acid - Weak Base System

A simple system for good removal of cations and most anions is treatment by a strong acid resin in the hydrogen form followed by a weak base resin in the free base form. Cations are effectively removed giving an acid solution of the anions. Anions forming strong acids are then removed on the weak base resin. Silicate and bicarbonate are not removed. Bicarbonate can, be removed, however, by air stripping. At the low pH it is removed as carbon dioxide. If it is necessary to remove silica, a strong base resin must be added at the end of the system. The cation resin is regenerated by a strong acid and the anion resin by either a weak or strong base.

The regenerant requirements depend upon the ion concentration to be removed from the feed water. In the usual application of this system the cost of regenerants would be rather high. A method of recovering the chemicals for reuse might result in a sizable saving. A system using nitric acid and ammonia has been proposed for carrying out recovery. After regeneration there would result a waste solution of nitrate salts from the cation exchange column and a solution of ammonium salts from the anion exchange column. By evaporation of the nitrate solution and steam calcination of the residue the nitric acid would be recovered. The mixture of hydroxides left after calcination would then be used in a lime still to recover ammonia. The degree of recovery of nitric acid is important to process economics.

Investigation has shown that nitrate salts of calcium, magnesium, aluminum, and iron calcine to give a good yield of acid. Sodium and potassium nitrates do not calcine well. The economics of the process are not well defined, but would depend upon the nature of the feed water.

B DESAL Process

Although regenerant recovery would appear to offer the lowest eventual ion exchange costs, systems that use a minimum of low cost regenerant would represent a substantial savings over the usual methods of ion exchange operation. A system that does use a minimum of regenerants has been proposed by the Rohm and Haas Company (3). This system is shown in Figure 2. It uses weak acid and base resins that can be regenerated with almost stoichoimetric amounts of chemicals. It can be used to treat waters of widely varying composition. Feed water enters a column of anion resin, IRA-68, in the bicarbonate form where anions other than bicarbonate are exchanged. The bicarbonate solution then enters a column of acid resin, IRC-84, in the hydrogen form where cations are exchanged. Because the solution is alkaline this exchange will take place. The carbon dioxide solution that results enters another anion exchange column in the free base form. The carbon dioxide converts this column to the bicarbonate form. When the resins are exhausted the first column in the series is regenerated to the free base form with ammonium hydroxide solution and the cation resin is regenerated to the hydrogen form. If the direction of flow is reversed the exhaustion cycle can be repeated since the third column is already in the bicarbonate form. The ammonia regenerant can be recovered by reacting with lime if desired. Columns in the bicarbonate form must be kept under a pressure of several atmospheres.

The resin IRA-68 has a high capacity for organic materials. A sample of the resin has been used to treat sand filtered secondary effluent through a number of exhaustion cycles. Roughly 50 percent

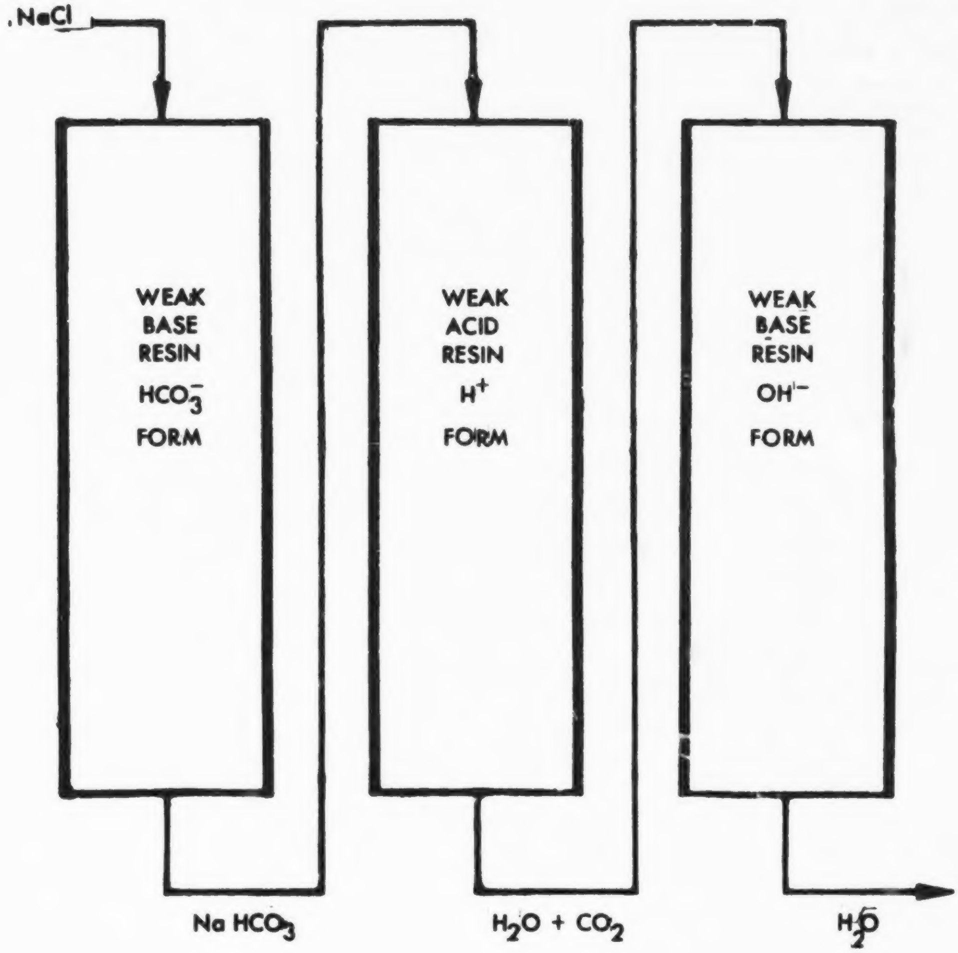
NaCl
WEAK BASE RESIN HCO_3^- FORM
WEAK ACID RESIN H^+ FORM
WEAK BASE RESIN OH^- FORM
Na HCO_3
$H_2O + CO_2$
H_2O

Figure 2. DESAL Process

of the organics measured by organic carbon is removed. Although the long term effect of the organics can only be determined through extended use, available results indicate that the organic contaminants are effectively removed during regeneration. The ability, not only to resist fouling by organics, but to adsorb a significant fraction of them is an example of the advances that have been made in resin technology.

IV OPERATING PROBLEMS

A number of problems common to electrodialysis also occur in ion exchange. Fouling of anion resins by organics and some inorganics is well known. Some of the newer resins are designed to overcome fouling. These may be used for removal of traces of organics from water. Generally, however, it is considered desirable to have the feed water as free from suspended matter and soluble organics as possible to lengthen resin life. Scaling may occur upon regeneration of cation resins with sulfuric acid when there are calcium ions on the resin ion. If too strong an acid solution is used, calcium sulfate will precipitate. Precipitation does require enough time that it can be avoided if regeneration is carried out properly.

V APPLICATION TO WASTEWATERS

A Municipal

There are two applications to municipal wastewater that may be useful. One application is the removal of the increment of minerals added during use. This could be carried out by completely demineralizing a fraction of the water, often about 40 percent, and mixing the demineralized water with untreated water. It might also be carried out by partial demineralization of the whole stream. The latter method would be most appropriate with continuous countercurrent equipment. Obviously both cation and anion exchange would be required. Pretreatment would probably be determined primarily by the use to be made of the treated water. With the older types of resin clarification and some degree of organic removal would probably be necessary. Less pretreatment should be required for the newer low-fouling resins.

The second use is for selective removal of certain ions, especially ammonium, nitrate, and phosphate. Removal of these nutrient materials is becoming increasingly necessary for control of algae growth in lakes and streams. Eliassen and coworkers (4) have investigated the use of anion exchange with sodium chloride regeneration for anion nutrient removal. This is not selective ion exchange in a strict sense since all anions except chloride would tend to be removed. In this work sand filtered secondary effluent was fed to the ion exchanger. Removals of phosphorus and nitrate were 84 and 77 percent respectively.

Little work has been done on truly selective removal of these materials, but a study is underway on ammonium ion removal. Certain natural zeolites have a high affinity for ammonium compared to most other cations in wastewater. An attempt will be made to develop a workable process from one of the zeolites. Hopefully, regeneration of the ion exchanger with lime will be possible. No highly selective material for nitrate removal is known. There is no reason, however, to believe that such a resin cannot be prepared. It may be of considerable value in the future. Phosphate is generally preferentially removed by anion exchange, but the situation with this material is not as critical as for the other nutrients because of the availability of other proven removal methods.

B Industrial

The use of ion exchange in industrial wastewater treatment has been very limited. With the growing need for industrial pollution control, applications may increase. Although electrodialysis and other processes could be strong competitors, there are certain instances where ion exchange should be most suited. These are situations in which small amounts of valuable or very harmful materials must be removed to very low levels. These may be the only contaminants present or there may be a mixture. The amount of regenerant required should be small. If selective removal from a mixture is required, ion exchange offers the most promise through development of selective resins or appropriate regeneration procedures. In the metal plating industry there are a number of instances in which ion exchange is presently used to remove small amounts of heavy metals from wastewaters. Examples are treatment of the rinse waters from copper, nickel, and chromium plating. At the same time as metal ions are recovered that would otherwise be lost, the quality of the water is improved. Often the product water is reused in the plating system. A rather recent application for ion exchange treatment of wastewater is for removal of radioactive ions from nuclear wastes. The method can be made to give a high degree of decontamination.

Although there are no known instances in which ion exchange is used for the general removal of an increment of total dissolved solids from industrial wastes as would be required for treatment of domestic wastes, such treatment may be necessary in some locations in the future. A study of each particular case will be required to determine whether ion exchange is the most economical treatment method.

VI ULTIMATE DISPOSAL OF CONCENTRATED WASTES

Ion exchange produces a significant amount of waste in the form of backwash water, spent regenerant, and rinse water. In most applications of the process little thought is given to minimizing the volume of waste. Where pollution control is of primary concern everything possible must be done to decrease this volume. The minimum volume of waste that might result from a properly designed and operated wastewater treatment system cannot be accurately estimated because of lack of data. Using manufacturers' recommendations the amount is quite large. For a commonly used cation resin the manufacturer suggests at least 60 gal/ft^2 bed cross-sectional area for backwash. If the ion exchange system is preceded by a solids-removal treatment, the backwash could be recycled back through that treatment. Using the usual concentrations of acid regenerant, the spent regenerant volume would be at least one percent of the feed for a mineral concentration typical of municipal wastewater. Naturally, more concentrated waters would require more regenerant. For regenerant rinse 150 gal/ft^3 resin is suggested. Again the volume of rinse depends upon the water concentration since this effects the resin volume. For a municipal wastewater the rinse water would be 5 to 10 percent of the feed. Obviously, for a system of cation and anion exchangers the volume of waste would be large. Reduction would undoubtedly be possible if restrictions were placed upon waste disposal.

VII OPERATING COSTS

In the past ion exchange has not been a cheap process to operate. Costs were often in the same range as distillation, more than \$1.00/1000 gal. For wastewater treatment in many cases such a cost does not appear competitive with the projected costs of other processes that are being developed. Through improved resins, improved design of equipment, and possibly regenerant recovery it is believed, however, that the cost of the process can be substantially reduced. Work on nutrient removal by anion exchange, for example, resulted in an estimated cost of 17-19¢/1000 gal. Experimental work presently being conducted should provide further cost information. For selective removal of a specific ion, ion exchange generally has no competitors. In these cases recovery of a valuable material is usually possible. Relatively high treatment cost may, therefore, be tolerable.

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